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## NEW DIRECTIONS IN PHTHALOCYANINE PIGMENTS

FINAL REPORT  
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### OBJECTIVES

1. Investigation of the synthesis of new phthalocyanines.
2. Characterization of the new phthalocyanines synthesized.
3. Investigate the properties of the newly synthesized phthalocyanines with emphasis on UV protection of plastics and coatings.
4. Utilize quantum mechanics to evaluate the structural relationships with possible properties and synthetic approaches.

The proposed research targeted the synthesis of phthalocyanines containing an aromatic bridge between two phthalocyanine rings. The goal was to synthesize pigments which would protect plastics when exposed to the photodegradation effects of the sun in space. The stability and extended conjugation of the phthalocyanines offer a unique opportunity for energy absorption and numerous radiative and non-radiative energy loss mechanisms. Although the original targeted phthalocyanines were changed early in the project, several new and unique phthalocyanine compounds were prepared.

The basic goals of this work were met and some unique and unexpected outcomes of the work were the result of the integral use of quantum mechanics and molecular modeling with the synthetic effort.

We are very pleased to present the following results.

(NASA-CR-192443) NEW DIRECTIONS IN  
PHTHALOCYANINE PIGMENTS Final  
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## RESULTS AND DISCUSSION

The first phthalocyanine synthesis attempted was that of Compound 3 which was to be prepared according to the method shown below. The initial attempts to synthesize the bisphthalocyanine using perylene-3,4:9,10-tetracarboxylic acid dianhydride as the core has resulted in only the formation of an amide type product Compound 4. Several variations in the synthetic approach yielded only Compound 4. Initial theories included the possibility of too much steric hindrance near the perylene core or the pi system is unstable.

The stability of the aromatic ring system of Compound 3 was in question, therefore AMPAC was employed to compare the heat of formation and ionization potential of the two model compounds shown below. Here a naphthalene ring is incorporated such that one is in a normal 5 membered ring, Compound 5, while Compound 6 has the same six membered ring that perylene would have. Compounds similar to Compound 5 have been synthesized and are stable. Compound 6, however, has to date never been synthesized. Based upon the very similar ionization potential(I.P.) and heats of formation(H.F.) they both should be stable and able to be synthesized.

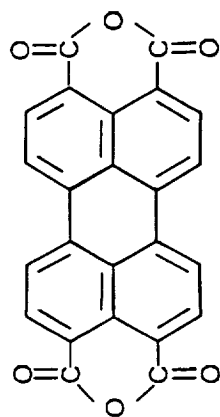
Phthalic anhydride and naphthalene 1,8-dicarboxylic acid were reacted with urea in an attempt to produce Compound 6. The reaction produced a dark colored material contaminated with Compound 7, phthalocyanine blue. Thus no new phthalocyanine was produced in a detectable amount. The reaction was apparently somewhat inhibitory to the formation of Compound 7 also since its yield was less than expected.

In an effort to understand the absence of Compound 6 in the reaction, AMPAC was used to evaluate the intermediates which are involved in the formation of phthalocyanines. The application of MNDO calculations to Compound 5 & 6 are given below.

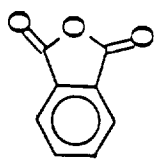
The following calculation was on a model compound using a single naphthalene unit as a prototype for the perylene structure. Further analysis will require careful examination of the bond order matrix.

Compound 6 - mono-1,8-naphthalene phthalocyanine  $C_{36}H_{20}N_8$

HEAT OF FORMATION = 273.994899 KCAL  
GRADIENT NORM = .428630  
DIPOLE = 8.50378 DEBYE  
NO. OF FILLED LEVELS = 102  
IONIZATION POTENTIAL = 6.933565 EV  
MOLECULAR WEIGHT = 564.608  
SCF CALCULATIONS = 1129  
COMPUTATION TIME = 9683.07 SECONDS  
GRADIENTS GNORM=0.1 T=18000 BONDS XYZ

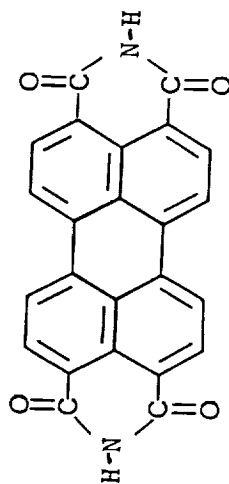
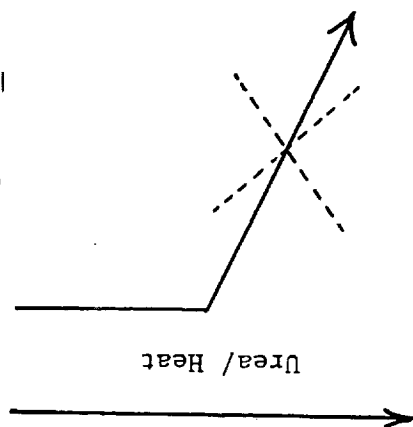


Compound 2

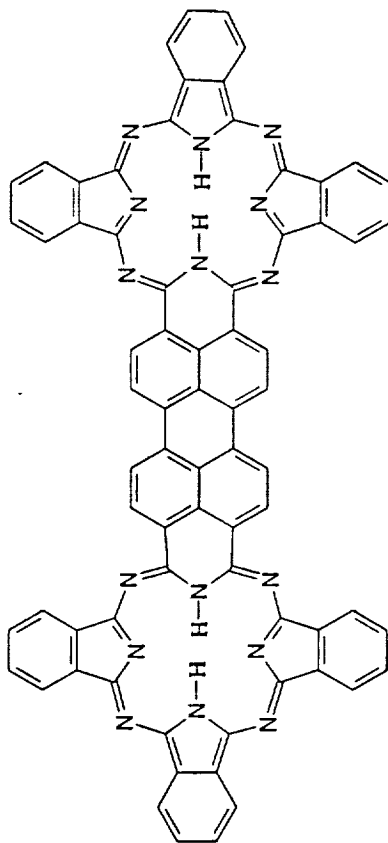


Compound 1

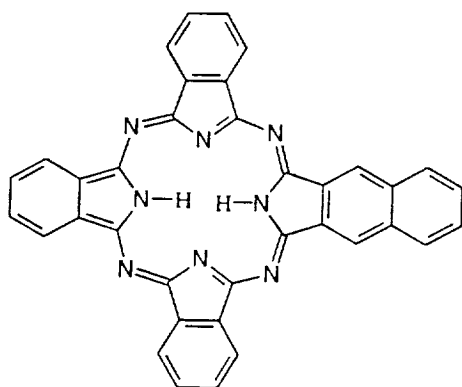
+



Compound 4



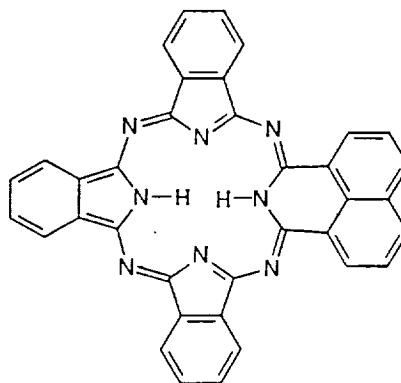
Compound 3



Compound 5

H.F. = 274.11 Kcal

I.P. = 6.995 EV



Compound 6

H.F. = 273.99 Kcal

I.P. = 6.934 EV

The following structure is similar to the above molecule except the naphthalene ring is in the conventional orientation.

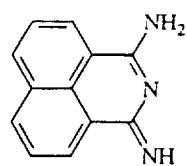
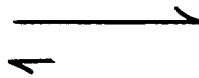
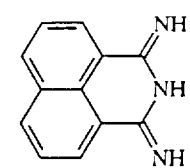
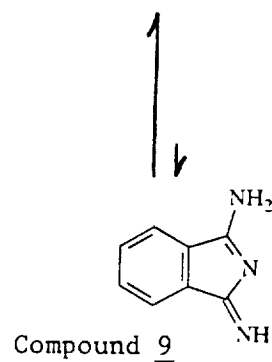
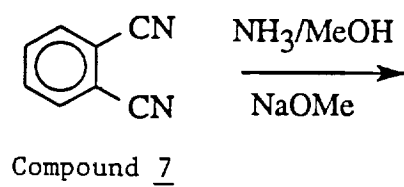
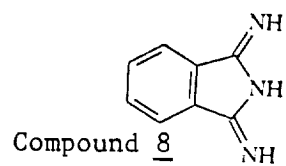
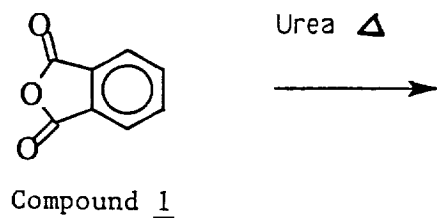
Compound 5 - mono-2,3-naphthalene phthalocyanine  $C_{36}H_{20}N_8$

HEAT OF FORMATION = 274.109605 KCAL  
GRADIENT NORM = .516983  
DIPOLE = 7.72256 DEBYE  
NO. OF FILLED LEVELS = 102  
IONIZATION POTENTIAL = 6.994719 EV  
MOLECULAR WEIGHT = 564.608  
SCF CALCULATIONS = 814  
COMPUTATION TIME = 7214.91 SECONDS  
GRADIENTS GNORM=0.1 T=72000 BONDS DENSITY XYZ  
PTHALOCYNINE Naphthalene in the normal mode

The synthesis of phthalocyanines has been investigated by numerous research groups. The key intermediate which has been found to be critical in phthalocyanine formation is Compound 8. It can be formed from phthalic anhydride (Compound 1) reacting with urea or 1,2-dicyanobenzene (Compound 7) reacting with ammonia. The best method for preparation is through 1,2-dicyanobenzene. The intermediate Compound 8 can have a tautomer Compound 9. Compound 9 has never been observed which implies that Compound 8 is more stable than Compound 9. Some researchers have believed that the observed spectra is really an average of the two tautomers and that the tautomerism is very rapid. We have investigated their stability through AMPAC calculations. In addition, we have also calculated the two tautomers for the naphthalene case, Compounds 10 and 11.

Below are the results of optimization for two possible phthalocyanine intermediates, Compound 8 and 9 and Compound 10 and 11, by MNDO to GNORM=0.5 level. The structural assignment was set by first using SYBYL to define the coordinate input to AMPAC and then optimized by AMPAC. These two structures and their tautomers are key intermediates in the synthetic process. It should be noted that Compound 8 is of lower energy than Compound 9 by 3.018 Kcal. However, Compound 10 is less stable than Compound 11 by 1.234 Kcal. This would imply that their chemistry may also be different. The synthetic attempts using the precursor to Compound 10 ie. the anhydride, did not produce phthalocyanine but the precursor to Compound 8 did. To determine if this energy difference which favored the alternate tautomer was generally applicable for all 1,9-naphthalene systems, several different mono and disubstituted versions of Compounds 10 and 11 were evaluated using AMPAC.

The AMPAC program has been used to evaluate various substituted naphthalene imide bisimine's as to the stability of it versus its tautomer. The theory of the intermediate being the cause for the inability of these type compounds to form phthalocyanine like systems may indeed be true. We may be able to use a substituted naphthalene system to gain a synthetic



advantage. The object is to find the best group or groups which destabilized the tautomer relative to the parent bisimine. If the theory is correct the new naphthalene system should form the phthalocyanine. These calculations are producing very interesting results.

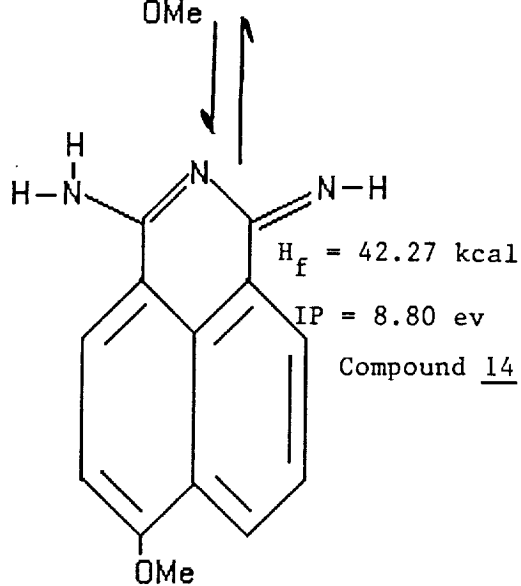
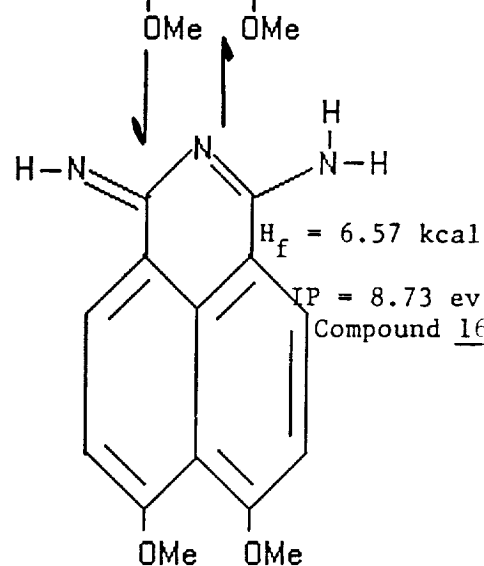
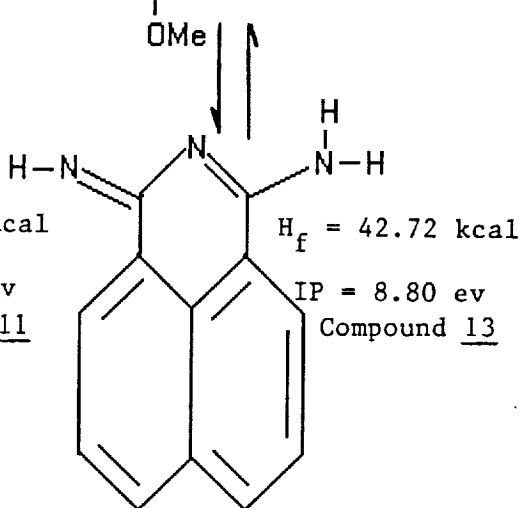
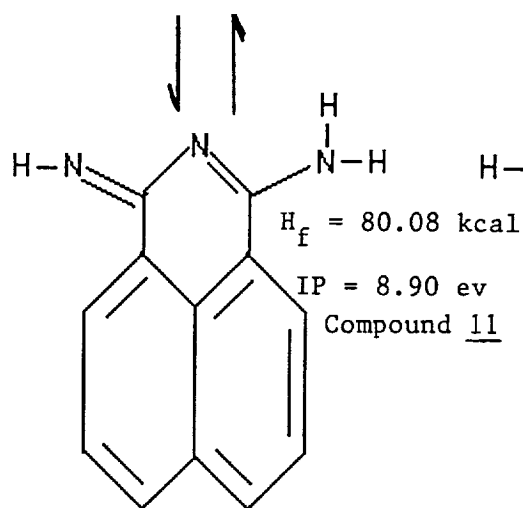
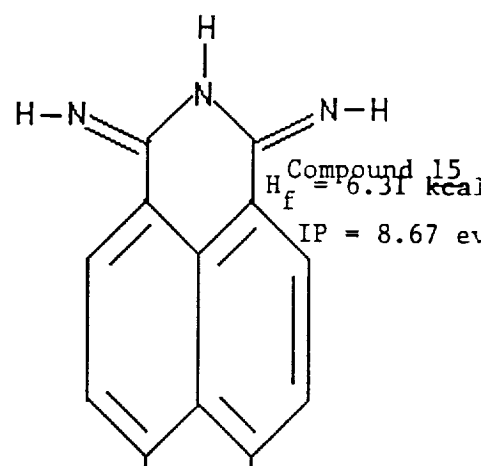
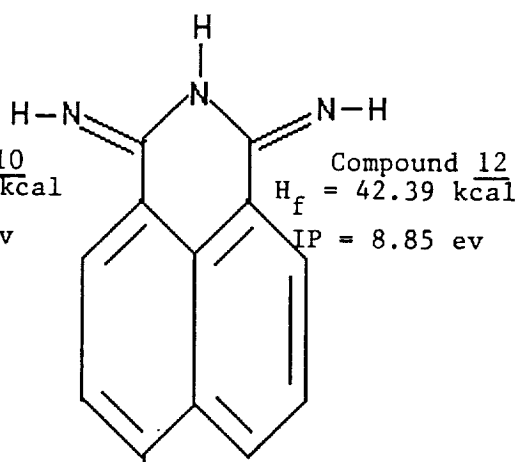
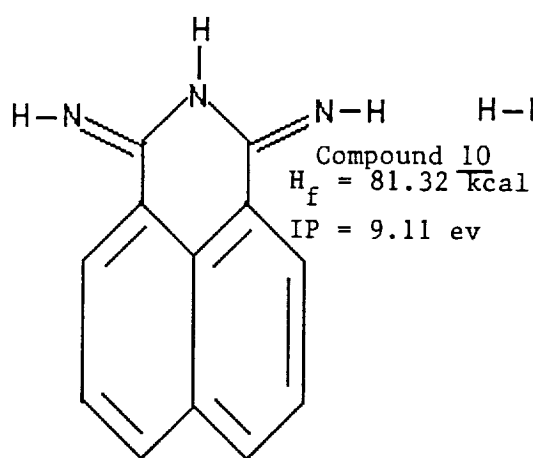
We have used AMPAC to evaluate various substituted naphthalene imide bisimine's as to the stability of it versus its tautomer. The theory of the intermediate being the cause for the inability of these type compounds to form phthalocyanine like systems may indeed be true. We may be able to use a substituted naphthalene system to gain a synthetic advantage. The object is to find the best group or groups which destabilized the tautomer relative to the parent bisimine. If the theory is correct the new naphthalene system should form the phthalocyanine. These calculations have produced very interesting results as can be seen from the attached pages of structures and data. We have chosen for this report only a subset of the data AMPAC provides us with. The values of heat of formation and ionization potential are shown for each structure. We have reached a valid level of optimization for each structure. The results given are for MNDO calculations at GNORM= 0.1. The confidence level for this type of calculation for similar structures is quite high. The substituents examined here are methoxy, fluorine, and hydrogen.

As can be seen in the heats of formation,  $H_f$ , and the ionization potential, IP, given on the following three pages for Compounds 12-23, only the difloro substituted structure produces a heat of formation for the bisimine which is lower in energy than the other tautomers. The lower energy finding is a critical piece of information in our synthetic design. It implies that only the difloro system should produce the phthalocyanine if the bisimine is the key intermediate. We are investigating ways to approach the synthesis of the difloro compound for future work, however, this synthesis may prove to be a significant undertaking.

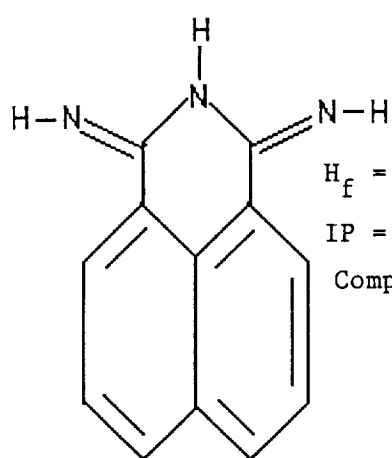
To test if Compound 10 or Compound 11 is the most stable its synthesis via the commercially available naphthalimide, Compound 24, was attempted as shown below. Numerous attempts were made with only starting material being isolated from the first step. This synthetic pathway has been used successfully to convert phthalimide to 1,2-dicyanobenzene, Compound 7.

The question of why this reaction does not work with the naphthalene analog was addressed again with AMPAC. The AMPAC program was used to determine the differences between the starting materials and products as compared to phthalimide, Compound 27. It can be readily seen from the data shown below that the phthalimide should proceed but that of naphthalimide should not.

The above finding may imply that the formation of the intermediate may be as problematic as the two tautomers Compounds



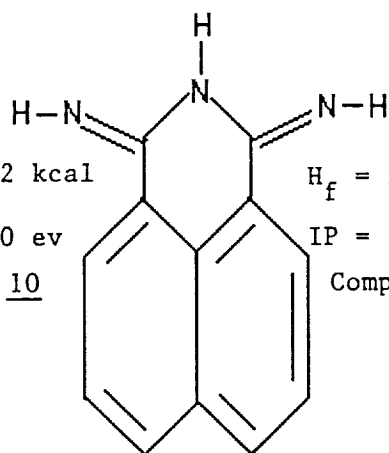




$H_f = 81.32 \text{ kcal}$

IP = 9.110 eV

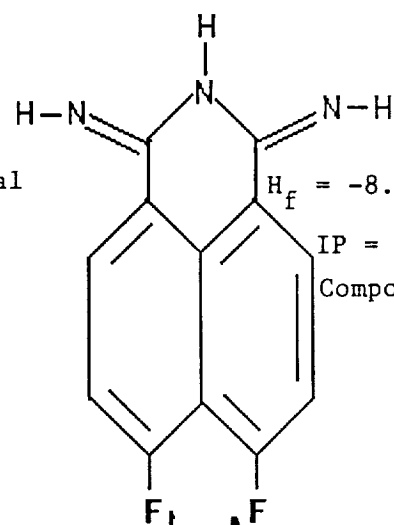
Compound 10



$H_f = 35.36 \text{ kcal}$

IP = 9.09 eV

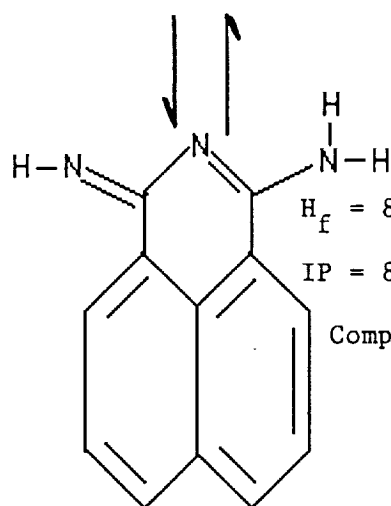
Compound 17



$H_f = -8.26 \text{ kcal}$

IP = 9.92 eV

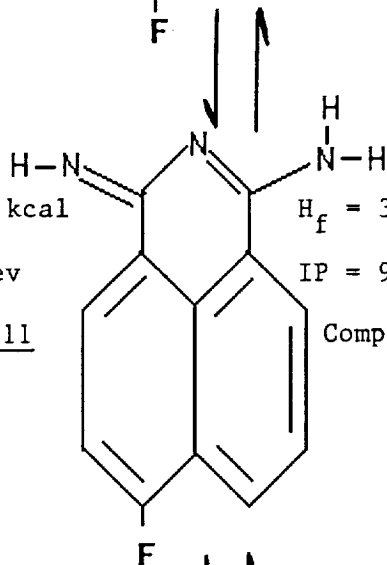
Compound 20



$H_f = 80.08 \text{ kcal}$

IP = 8.90 eV

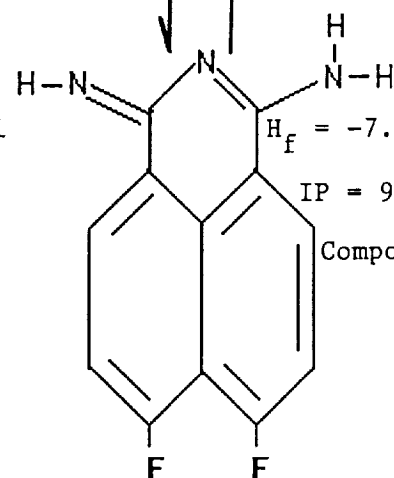
Compound 11



$H_f = 35.70 \text{ kcal}$

IP = 9.02 eV

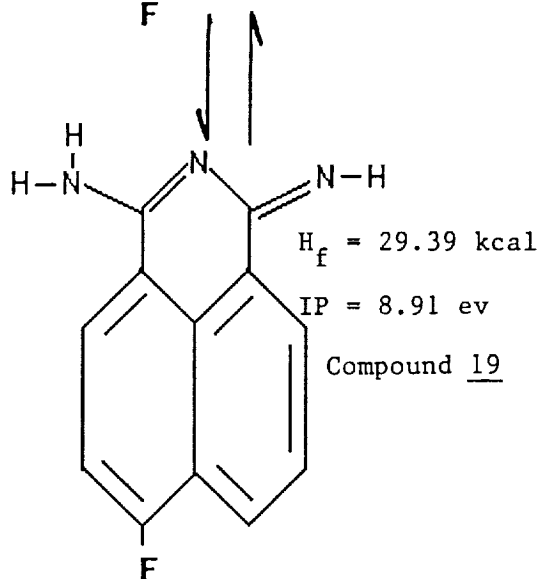
Compound 18



$H_f = -7.98 \text{ kcal}$

IP = 9.13 eV

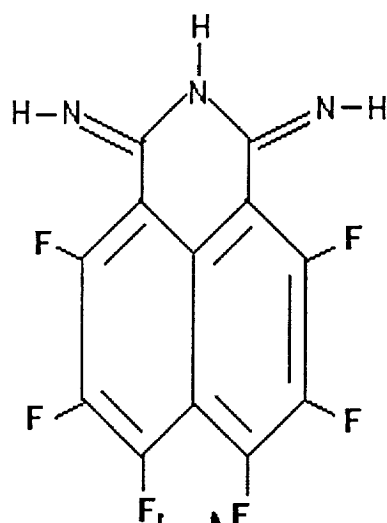
Compound 21



$H_f = 29.39 \text{ kcal}$

IP = 8.91 eV

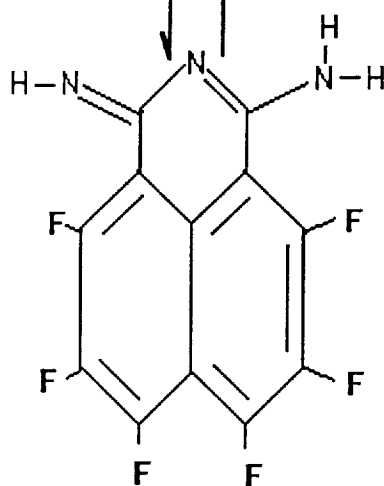
Compound 19



Compound 22

$H_f = -174.85$  kcal

IP = 10.126 eV

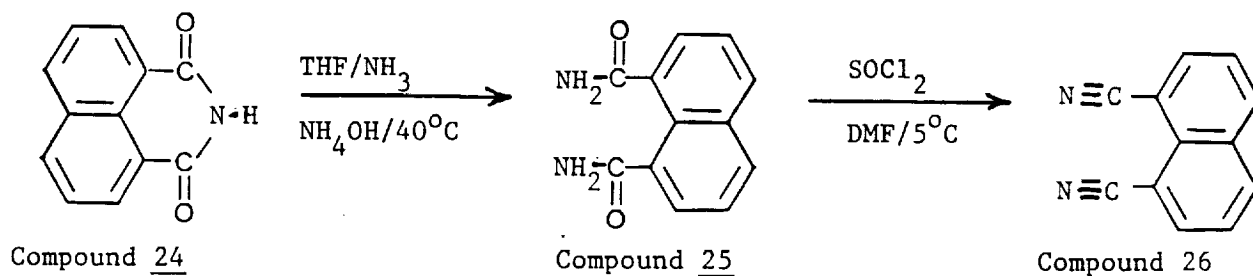


Compound 23

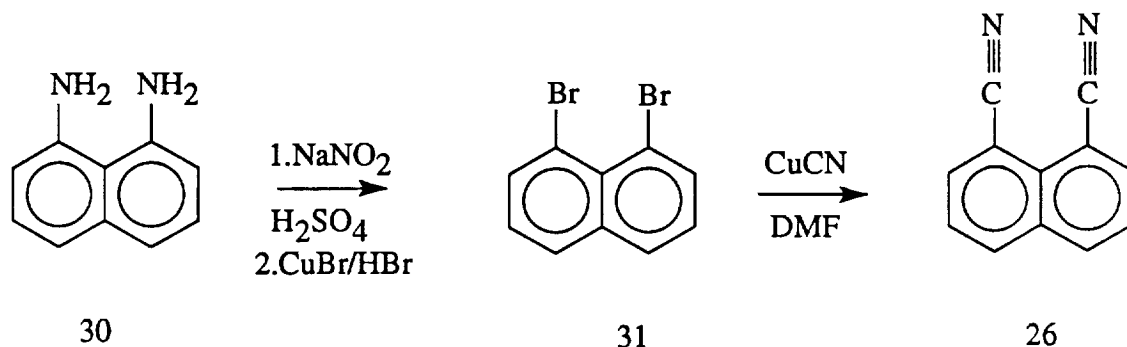
$H_f = -177.44$  kcal

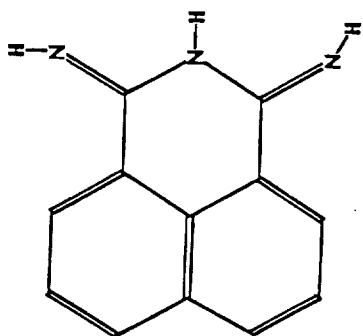
IP = 9.599 eV

10 and 11. We have synthesized 1,8-dicyanonaphthalene through the Sandmeyer reaction. This method involves converting 1,8-diaminonaphthalene to the bidiazonium salt and reaction with copper bromide and hydrogen bromide to give 1,8-dibromonaphthalene, Compound 31. The dibromide is then purified and reacted with copper cyanide in N,N-dimethylformamide which produces 1,8-dicyanonaphthalene, Compound 26. The overall yield for this process is extremely low and the process is laborious. This process was however used successfully to produce the 1,8-dicyanonaphthalene.



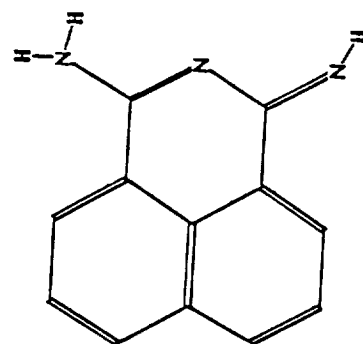
The conversion of 1,8-dicyanonaphthalene, Compound 26, to the key intermediate, Compound 10/11, was accomplished by bubbling ammonia through a methanol/1,2-dimethoxyethane solution of Compound 26 with a catalytic amount of sodium. The reaction proceeded rapidly and produced a clean product with only minor impurities. The product was chromatographed on alumina to produce a pure product, Compound 11. The AMPAC calculations were borne out in the prediction that Compound 11 would predominate over Compound 10. It should be noted that not only is this a significant finding in its self but the question of whether the tautomerism is rapid on an NMR time scale has been questioned and indeed if the two tautomers were rapidly exchanging the spectra would not appear as it does. There would be only two multiplets and no peak at 8.6 delta as was observed for Compound 11.





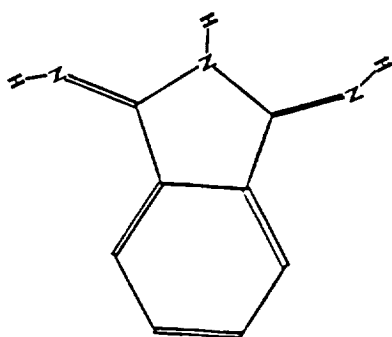
Compound 10

MNDO RHF:  $\Delta H = 79.493$  KCAL  
 IP = 8.861 EV  
 MNDO UHF:  $\Delta H = 71.523$  KCAL  
 IP = 9.283 EV  
 AM1 UHF :  $\Delta H = 91.224$  KCAL  
 IP = 9.110 EV  
 AM1 RHF :  $\Delta H = 93.575$  KCAL  
 IP = 8.881 EV



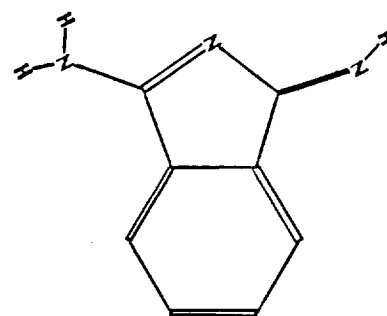
Compound 11

$\Delta H = 74.184$  KCAL  
 IP = 8.782 EV  
 $\Delta H = 64.123$  KCAL  
 IP = 9.066 EV  
 $\Delta H = 88.316$  KCAL  
 IP = 8.758 EV  
 $\Delta H = 92.353$  KCAL  
 IP = 8.745 EV



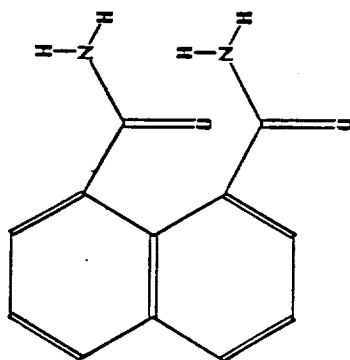
Compound 8

MNDO RHF :  $\Delta H = 65.901$  KCAL  
 IP = 9.622 EV  
 MNDO UHF :  $\Delta H = 63.267$  KCAL  
 IP = 9.743 EV  
 AM1 UHF :  $\Delta H = 85.752$  KCAL  
 IP = 9.590 EV  
 AM1 RHF :  $\Delta H = 85.923$  KCAL  
 IP = 9.565 EV



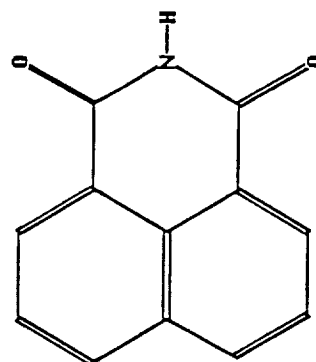
Compound 9

$\Delta H = 69.025$  KCAL  
 IP = 9.682 EV  
 $\Delta H = 66.586$  KCAL  
 IP = 9.788 EV  
 $\Delta H = 90.744$  KCAL  
 IP = 9.529 EV  
 $\Delta H = 90.744$   
 IP = 9.529 EV



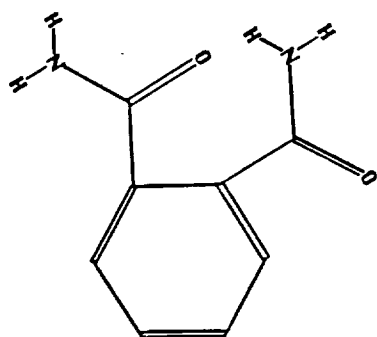
Compound 25

MNDO RHF :  $\Delta H = -25.512$  KCAL  
 IP = 9.134 EV  
 MNDO UHF :  $\Delta H = -33.326$  KCAL  
 IP = 9.542 EV  
 AM1 UHF :  $\Delta H = -27.298$  KCAL  
 IP = 9.383 EV  
 AM1 RHF :  $\Delta H = -25.314$  KCAL  
 IP = 9.172 EV



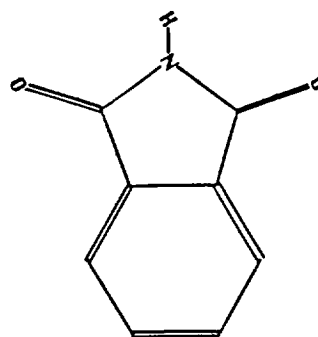
Compound 24

$\Delta H = -34.765$  KCAL  
 IP = 9.355 EV  
 $\Delta H = -41.429$  KCAL  
 IP = 9.700 EV  
 $\Delta H = -24.981$  KCAL  
 IP = 9.626 EV  
 $\Delta H = -23.600$  KCAL  
 IP = 9.484 EV



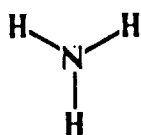
Compound 27

MNDO RHF :  $\Delta H = -49.674$  KCAL  
 IP = 10.069 EV  
 MNDO UHF :  $\Delta H = -51.705$  KCAL  
 IP = 10.335 EV  
 AM1 UHF :  $\Delta H = -54.025$  KCAL  
 IP = 10.207 EV  
 AM1 RHF :  $\Delta H = -54.007$  KCAL  
 IP = 10.198 EV



Compound 28

$\Delta H = -46.817$  KCAL  
 IP = 10.271 EV  
 $\Delta H = -48.657$  KCAL  
 IP = 10.497 EV  
 $\Delta H = -26.086$  KCAL  
 IP = 10.494 EV  
 $\Delta H = -26.085$  KCAL  
 IP = 10.480 EV



Compound 29

MNDO RHF :  $\Delta H = -6.051$  KCAL

IP = 11.192 EV

MNDO UHF :  $\Delta H = -6.051$  KCAL

IP = 11.192 EV

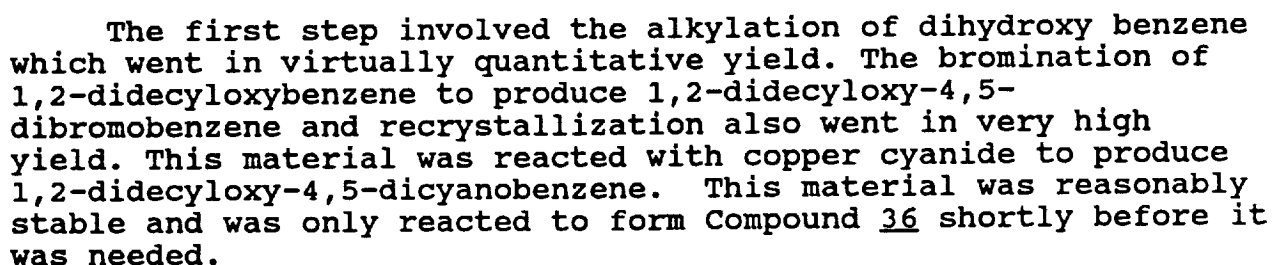
AM1 UHF :  $\Delta H = -7.283$  KCAL

IP = 10.421 EV

AM1 RHF :  $\Delta H = -7.283$  KCAL

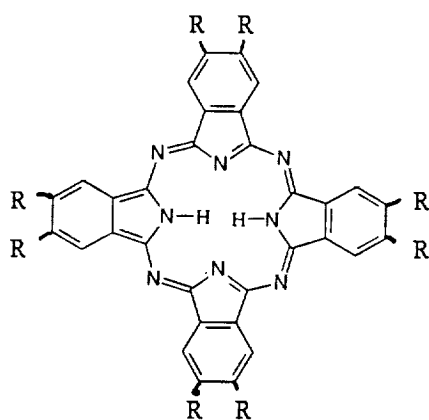
IP = 10.421 EV

NASA was unable to vacuum sublime the phthalocyanine products in a timely basis. Therefore, the research plan was altered to make the products soluble in solvents which would allow better purification of the phthalocyanines. To that end the following synthetic path to produce Compound 36 from 32 was undertaken. Compound with two long chains would allow all the compounds being synthesized to be soluble in solvents necessary to purify and characterize the materials.

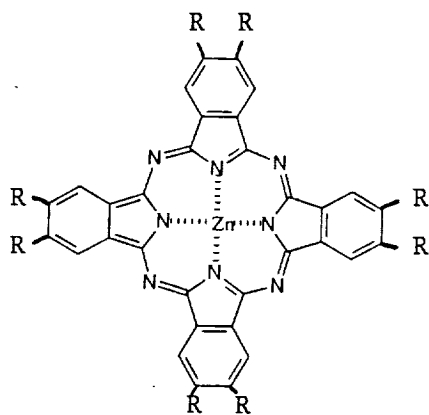
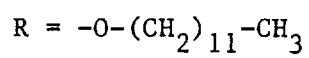


Compound 36 was then heated in 2-N,N-dimethylaminoethanol at 140°C to produce a green single ringed phthalocyanine, Compound 37. The same procedure was also repeated with zinc acetate present to produce the zinc metalated system, Compound 38. Both systems were chromatographed and spectra obtained. The non-metalated phthalocyanine will be an impurity in all synthetic preparations of the two ring systems and non-symmetric phthalocyanines. Therefore its characterization was critical and it is one of the compounds being evaluated for the UV protection of plastics.

The single ringed phthalocyanine, Compound 37 produced a spectra in good agreement with that from similar molecules in the literature. The spectra from Compound 38, the zinc containing phthalocyanine is also in excellent agreement. The Qx and Qy bands at 703 and 665 nm in Compound 37 are only one Q transition at 679 nm in Compound 38 since the  $D_{2h}$  symmetry of Compound 37 has become  $D_{4h}$  in Compound 38 resulting in only 1 transition ( $^1A_{1g}$  to  $^1E_u$ ).



Compound 37



Compound 38



1.000

ABS

-0.100

nm

Compound 38

400

600

800

PEAK			VALLEY	
NO.	nm	ABS	nm	ABS
1	679.0	0.727	631.0	0.072
2	613.0	0.121	526.0	0.014
3	355.0	0.446	314.0	0.220
4	294.0	0.323	284.0	0.300

1.000

ABS

-0.100

nm

Compound 37

400

600

800

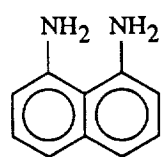
PEAK			VALLEY	
NO.	nm	ABS	nm	ABS
1	703.0	0.816	686.0	0.150
2	665.0	0.661	620.0	0.092
3	604.0	0.131	527.0	-0.002
4	427.0	0.192	382.0	0.121
5	350.0	0.501	311.0	0.225
6	297.0	0.338	280.0	0.213

## TETRAPHENYL PHTHALOCYANINES

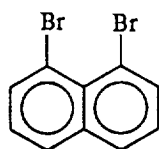
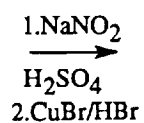
We have utilized tetraphenyl-phthalic anhydride, Compound 39, which was as shown below, with phthalic anhydride heated in urea to synthesize the first targeted phthalocyanine Compound 43. The synthesis of the octaphenylphthalocyanine shown below has presumably gone as anticipated and full confirmation of structure through spectroscopic analysis is consistent but purification is difficult. Absolute identification of the product as Compound 43 has not been made due to impurities. The product is green, unlike the parent which is blue. The blue color of the standard phthalocyanine is in part due to two phthalocyanines coupling through their pi systems. In the case of the octaphenylphthalocyanine the presence of the eight phenyls at a  $45^\circ$  angle precludes the approach to a coupling distance according to SIBYL modeling. The octaphenylphthalocyanine was sent to NASA for sublimation but difficulty in sublimation precluded its further purification. The distance between the planar rings will be of particular interest. We obtained Magic Angle Spinning NMR spectra of this compound to help confirm the structure. The use of Magic Angle spinning is required since the compound lacks solubility in any reasonable solvent. The spectra was consistent but lacked enough definition to be absolutely conclusive.

To increase the yield of tetraphenylphthalate incorporation and to ease the purification problem, Compound 48 was targeted. The approach was to make the key intermediate 47 from Compound 44. This approach went well from Compound 44 to 46. The last step went slowly and Compound 47 was found to be somewhat unstable. Compound 48 was prepared using the intermediate Compound 47 and Compound 36. The phthalocyanine, Compound 48 was the major product other than the expected Compound 37. The large steric hindrance of the tetraphenyl group reduces the amount of bis incorporation, Compound 43 with dodecyl chains. We have worked out separation techniques using normal and size exclusion chromatography to purify this material. The UV/Visible spectra of this material is shown below.

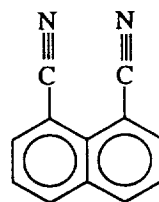
The above Compound 48 was then metalated with cobalt in toluene and purified Compound 48\*Co. The spectra below illustrates the collapse of the splitting and a spectral shift. It should be noted that this compound is much more blue than Compound 48.



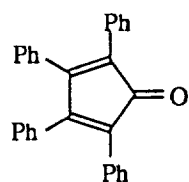
30



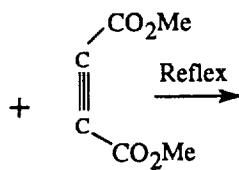
31



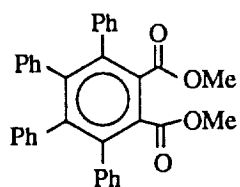
26



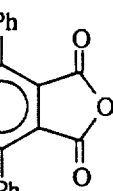
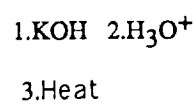
39



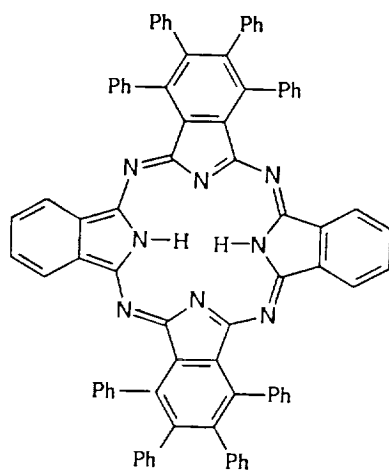
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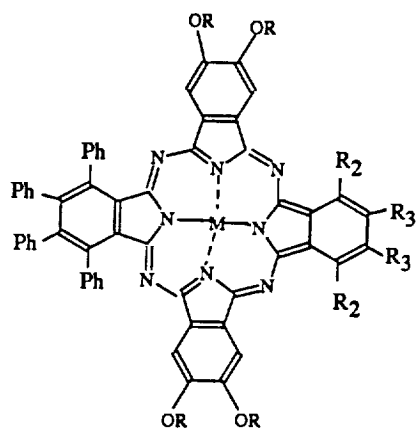
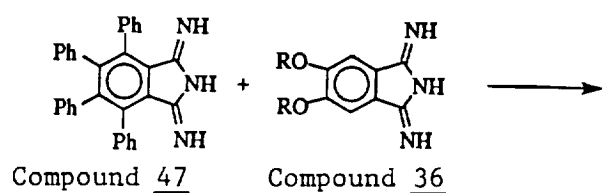
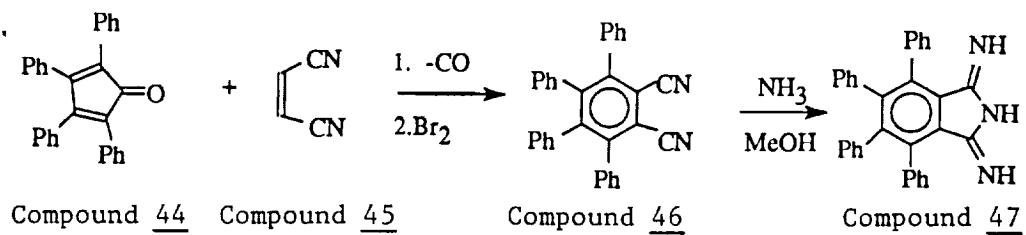
41



42



Compound 43

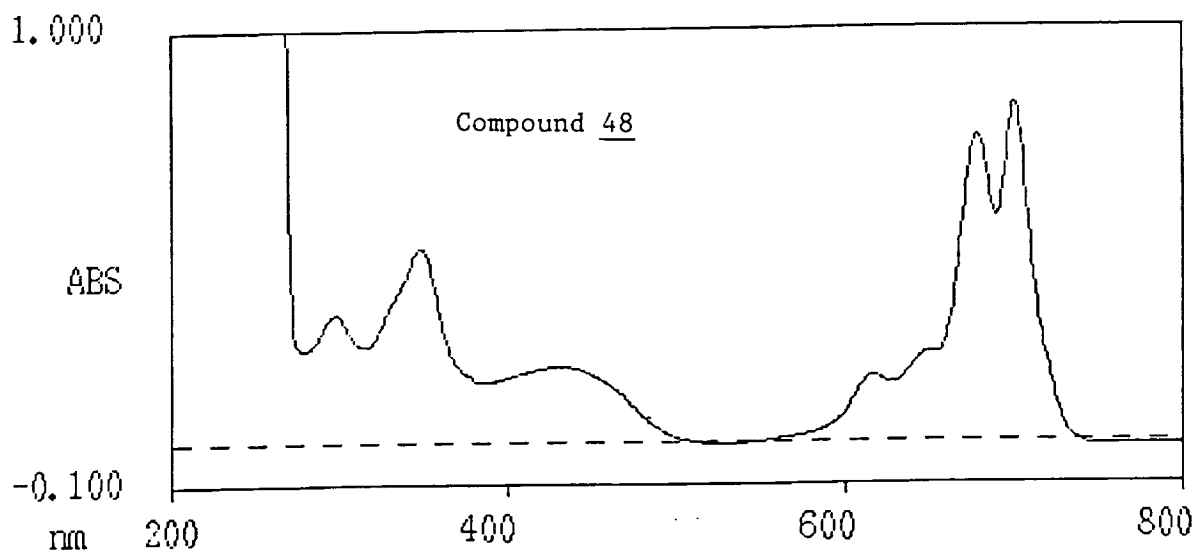


$R = C_{12}H_{25}$

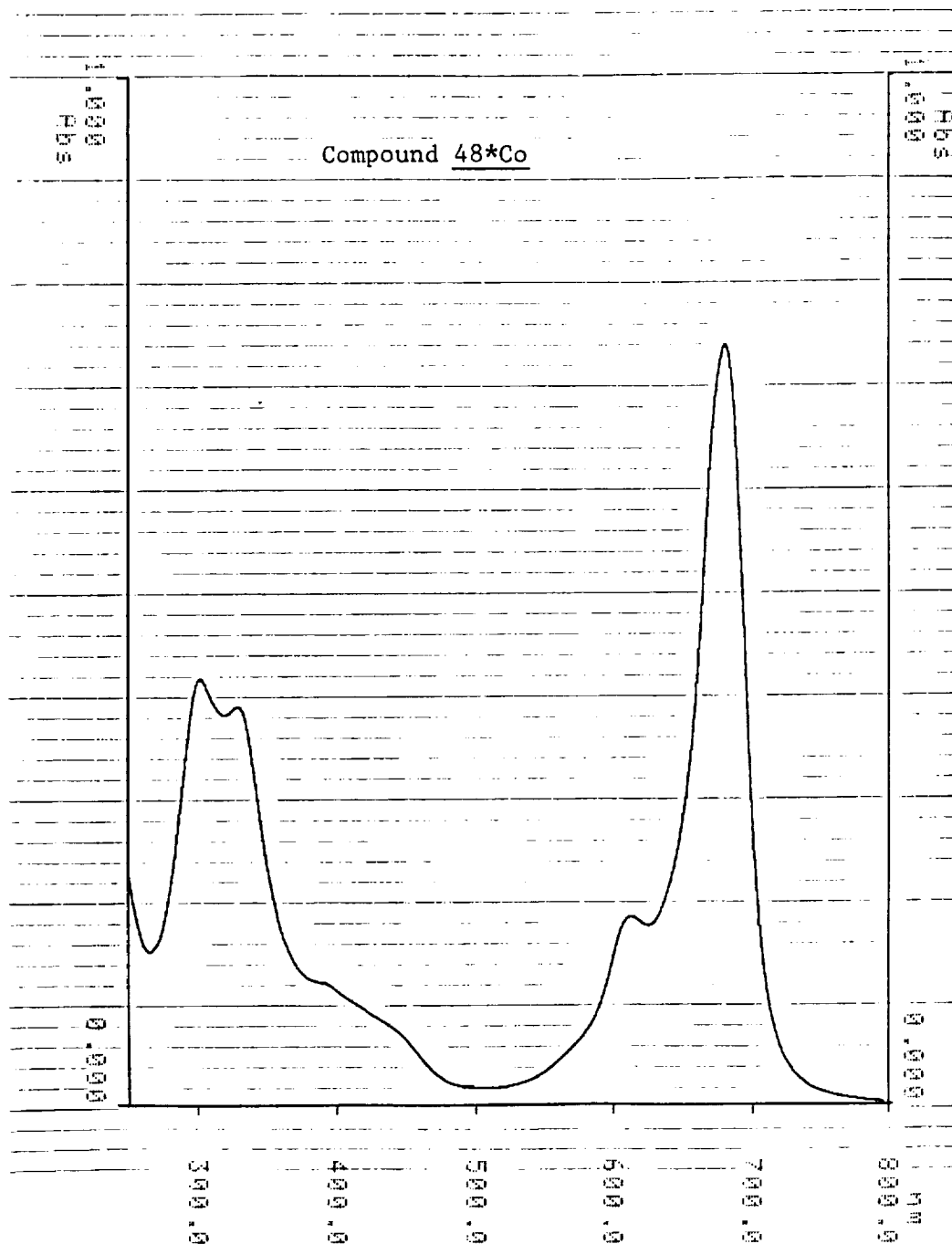
$M = H_2$

$R_2 = H, R_3 = OCH_{12}H_{25}$     Compound 48

$R_2 = R_3 = Ph$     Compound 48a



NO.	PEAK		VALLEY	
	nm	ABS	nm	ABS
1	700.0	0.816	689.0	0.545
2	678.0	0.740	627.0	0.143
3	615.0	0.162	525.0	-0.002
4	430.0	0.186	387.0	0.148
5	349.0	0.475	314.0	0.235
6	297.0	0.314	279.0	0.228



TITLE: TETRAPC(CO)  
 SCAN SPEED: 120.0 nm/min  
 BANDPASS: 2.00nm

9:33 PM 7/29/92  
 RESPONSE: MEDIUM

NO.	PEAK	VALLEY
1	679.6 nm 0.7372 Abs	625.2 nm 0.1735 Abs
2	613.2 nm 0.1818 Abs	566.4 nm 0.0159 Abs
3	328.8 nm 0.3876 Abs	320.4 nm 0.3794 Abs
4	302.4 nm 0.4145 Abs	265.6 nm 0.1497 Abs

## AMPAC CALCULATIONS ON PHTHALOCYANINES

We obtained the newest version of AMPAC a MNDO and AM1 quantum mechanical package used to determine the electronic energetics of a structure. The AMPAC program was installed on our Silicon Graphics computer and on the IBM 6000 RISC system. AMPAC has been verified as to it being in correct working order on the Silicon Graphics computer, however the memory limits of that computer will only allow 50 non-hydrogen atoms to be calculated. The targeted molecule has nearly 150 non-hydrogen atoms. We successfully ported AMPAC to the IBM-6000 which has six times the memory and approximately 6 times the speed of the Silicon Graphic Computer. The IBM allows a matrix of the full 150 atoms to be calculated.

Compounds 49 to 57 were molecularly modeled using either Sybyl or Alchemy and MNDO run to GNORM=0.1. The values for the heats of formation and ionization potential are given with the structures. The electron density matrix and bond order were calculated and indicate good stability for all the compounds. Therefore Compounds 49 to 57 should be stable if they can be constructed. It does not mean that using conventional techniques that they can be synthesized. Thus far we have been able to construct relatives of compounds 49, 50, 51, 52, 56, and 57.

Below are the results of optimization for phthalocyanine by MNDO to GNORM=0.5 level. The structural assignment which was set by first using SYBYL to define the coordinate input to AMPAC and then optimized by AMPAC. The agreement with coordinates are excellent. Thus the program is very useful and reliable.

### PHTHALOCYANINE C<sub>32</sub>H<sub>18</sub>N<sub>8</sub>

HEAT OF FORMATION = 258.441407 KCAL  
GRADIENT NORM = .546150  
DIPOLE = 6.54579 DEBYE  
NO. OF FILLED LEVELS = 93  
IONIZATION POTENTIAL = 7.031705 EV  
MOLECULAR WEIGHT = 514.548  
SCF CALCULATIONS = 704  
COMPUTATION TIME = 4964.57 SECONDS  
GRADIENTS GNORM=0.1 T=18000 BONDS XYZ

The following is a list of the atoms and their bond lengths and charges. They are all consistent with the x-ray structure.

### PHTHALOCYANINE

H	.000000	0	.000000	0	.000000	0	0	0	0	.2500
N	.998794	1	.000000	0	.000000	0	1	0	0	-.3493
C	1.410083	1	123.274504	1	.000000	0	2	1	0	.3216
C	1.490919	1	105.272354	1	-171.422793	1	3	2	1	-.0785
C	1.392891	1	131.552656	1	176.745284	1	4	3	2	.0194
H	1.089965	1	121.824595	1	-.454258	1	5	4	3	.0852

C	1.420394	1	118.347526	1	179.539485	1	5	4	3	-.0500
H	1.091072	1	119.047973	1	179.986936	1	7	5	4	.0706
C	1.398585	1	121.039694	1	-.036030	1	7	5	4	-.0499
H	1.091035	1	119.923550	1	-179.983607	1	9	7	5	.0706
C	1.420469	1	121.032944	1	-.007165	1	9	7	5	.0193
H	1.089950	1	119.826271	1	-179.943066	1	11	9	7	.0852
C	1.392879	1	118.360722	1	.047439	1	11	9	7	-.0783
C	1.410049	1	123.271596	1	-177.622484	1	2	1	3	.3215
N	1.304946	1	129.481435	1	-10.283670	1	14	2	1	-.2975
C	1.390894	1	126.278698	1	-3.972449	1	15	14	2	.2258
C	1.487877	1	123.205437	1	176.588227	1	16	15	14	-.0970
C	1.392105	1	134.063507	1	-2.391322	1	17	16	15	.0179
H	1.089571	1	121.848800	1	-.180035	1	18	17	16	.0747
C	1.418637	1	118.186206	1	179.791620	1	18	17	16	-.0689
H	1.090850	1	119.145540	1	-179.981660	1	20	18	17	.0635
C	1.400309	1	121.059488	1	-.001801	1	20	18	17	-.0465
H	1.091063	1	119.749755	1	-179.967749	1	22	20	18	.0638
C	1.419161	1	121.185197	1	.039258	1	22	20	18	-.0014
H	1.089607	1	119.958121	1	179.976404	1	24	22	20	.0802
C	1.392589	1	118.232935	1	-.013089	1	24	22	20	-.0549
C	1.489614	1	133.420450	1	179.707829	1	26	24	22	.1374
N	1.327737	1	125.164776	1	-6.015470	1	16	15	14	-.3500
N	1.303113	1	125.394391	1	-1.015780	1	27	26	24	-.1735
C	1.377829	1	127.430095	1	-178.034930	1	29	27	26	.0849
C	1.434558	1	125.793628	1	169.004139	1	30	29	27	-.0548
C	1.429561	1	132.833780	1	1.924553	1	31	30	29	-.0096
H	1.089654	1	120.087762	1	.359922	1	32	31	30	.0670
C	1.383207	1	118.919548	1	-179.822116	1	32	31	30	-.0700
H	1.091000	1	120.352888	1	-179.758491	1	34	32	31	.0547
C	1.435376	1	121.285091	1	.235642	1	34	32	31	-.0700
H	1.090862	1	118.345146	1	179.995505	1	36	34	32	.0546
C	1.383308	1	121.292493	1	-.015378	1	36	34	32	-.0095
H	1.089717	1	120.997717	1	179.956370	1	38	36	34	.0670
C	1.429607	1	118.921141	1	-.219604	1	38	36	34	-.0549
C	1.434618	1	132.876862	1	179.825074	1	40	38	36	.0851
N	1.394135	1	106.793445	1	179.321474	1	41	40	38	-.1646
H	.997840	1	124.007711	1	-172.236465	1	42	41	40	.2354
N	1.377948	1	125.814341	1	-1.890570	1	41	40	38	-.1736
C	1.303103	1	127.421565	1	-168.947802	1	44	41	40	.1376
C	1.489540	1	125.363889	1	178.087614	1	45	44	41	-.0550
C	1.392497	1	133.409538	1	1.023328	1	46	45	44	-.0013
H	1.089640	1	121.818556	1	.287947	1	47	46	45	.0802
C	1.419191	1	118.215595	1	-179.701601	1	47	46	45	-.0465
H	1.091119	1	119.048320	1	-179.990197	1	49	47	46	.0638
C	1.400311	1	121.190045	1	.032844	1	49	47	46	-.0689
H	1.090782	1	119.816805	1	179.961353	1	51	49	47	.0635
C	1.418710	1	121.064798	1	-.072158	1	51	49	47	.0179
H	1.089594	1	119.962208	1	-179.962995	1	53	51	49	.0747
C	1.392050	1	118.174891	1	.018248	1	53	51	49	-.0970
C	1.487911	1	134.061610	1	-179.771437	1	55	53	51	.2258
N	1.327761	1	111.589676	1	-179.890044	1	56	55	53	-.3500
N	1.304970	1	129.470943	1	10.332903	1	3	2	1	-.2976
O	.000000	0	.000000	0	.000000	0	0	0	0	



This structure is minimized with zinc as the center element for the standard phthalocyanine as defined using x-ray coordinates.

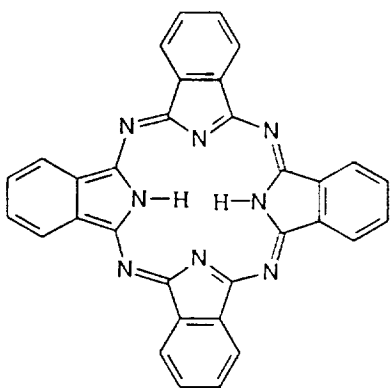
PHTHALOCYANINE-CO/ZN  $C_{32}H_{16}N_8Zn$

HEAT OF FORMATION = 253.641375 KCAL  
GRADIENT NORM = .066891  
DIPOLE = 5.99888 DEBYE  
NO. OF FILLED LEVELS = 93  
IONIZATION POTENTIAL = 6.683682 EV  
MOLECULAR WEIGHT = 577.912  
SCF CALCULATIONS = 260  
COMPUTATION TIME = 2480.54 SECONDS  
GRADIENTS GNORM=0.1 T=18000 BONDS DENSITY XYZ

The next structure is the bisphthalocyanine complexes with anthracene core. The results indicate that the structure should be relatively stable.

ANTH-DI-PHTHOLOCYNINE  $C_{66}H_{34}N_{16}$

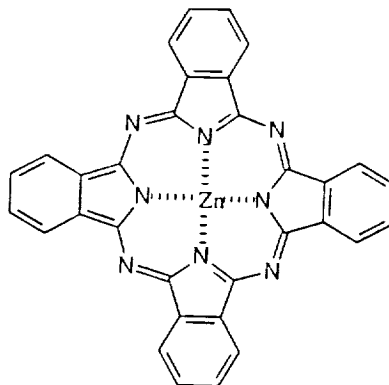
HEAT OF FORMATION = 541.250239 KCAL  
GRADIENT NORM = 19.548030  
DIPOLE = 17.97050 DEBYE  
NO. OF FILLED LEVELS = 189  
IONIZATION POTENTIAL = 6.842447 EV  
MOLECULAR WEIGHT = 1051.102  
SCF CALCULATIONS = 169  
COMPUTATION TIME = 15029.95 SECONDS  
GRADIENTS GNORM=20 BONDS T=18000 XYZ



Compound 49

H.F. = 258.44 Kcal

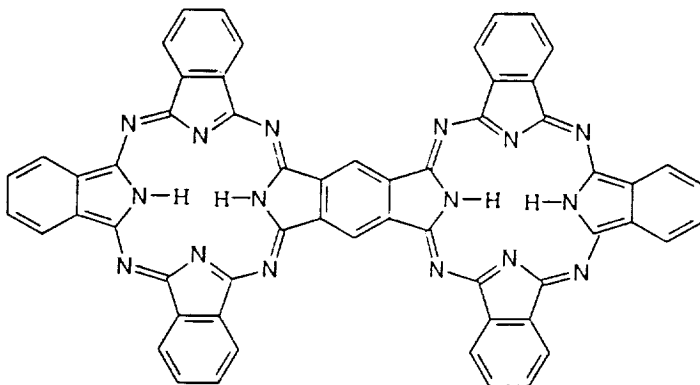
I.P. = 7.032 EV



Compound 50

H.F. = 253.64 Kcal

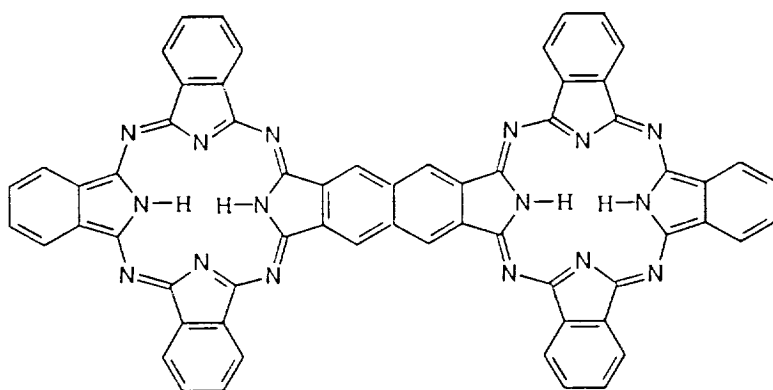
I.P. = 6.684 EV



Compound 51

H.F. = 498.68 Kcal

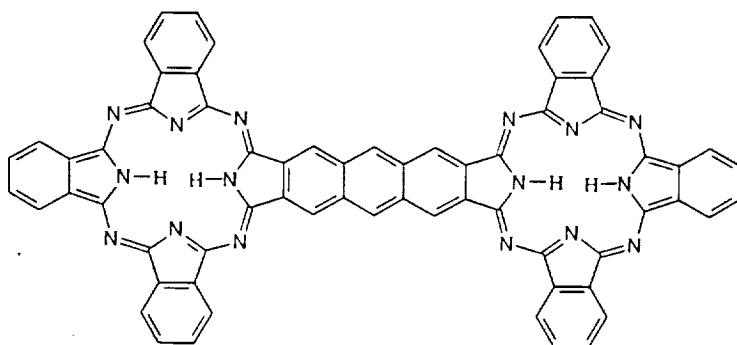
I.P. = 7.176 EV



Compound 52

H.F. = 512.35 Kcal

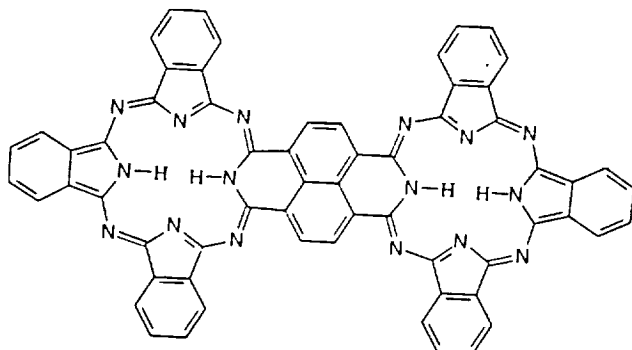
I.P. = 7.139 EV



Compound 53

H.F. = 535.35 Kcal

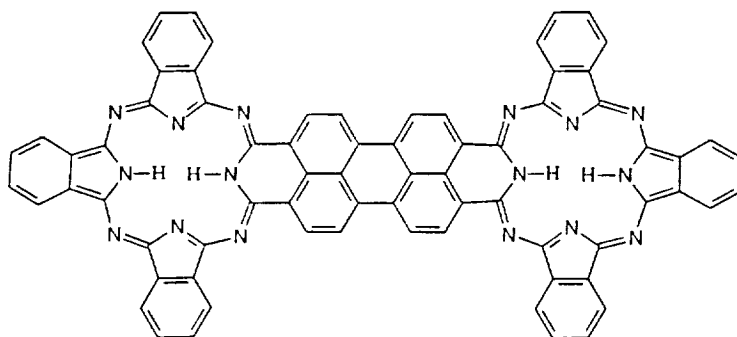
I.P. = 6.839 EV



Compound 54

H.F. = 513.17 Kcal

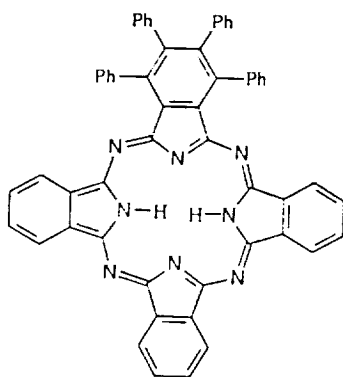
I.P. = 7.110 EV



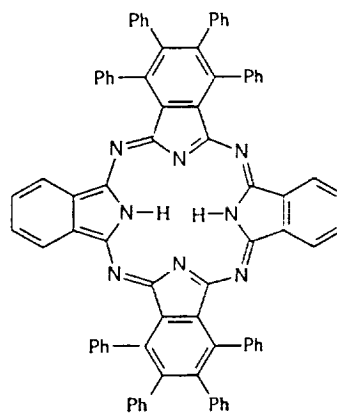
Compound 55

H.F. = 556.90 Kcal

I.P. = 7.050 EV



Compound 56



Compound 57

## SYNTHESIS OF BISPHTHALOCYANINES

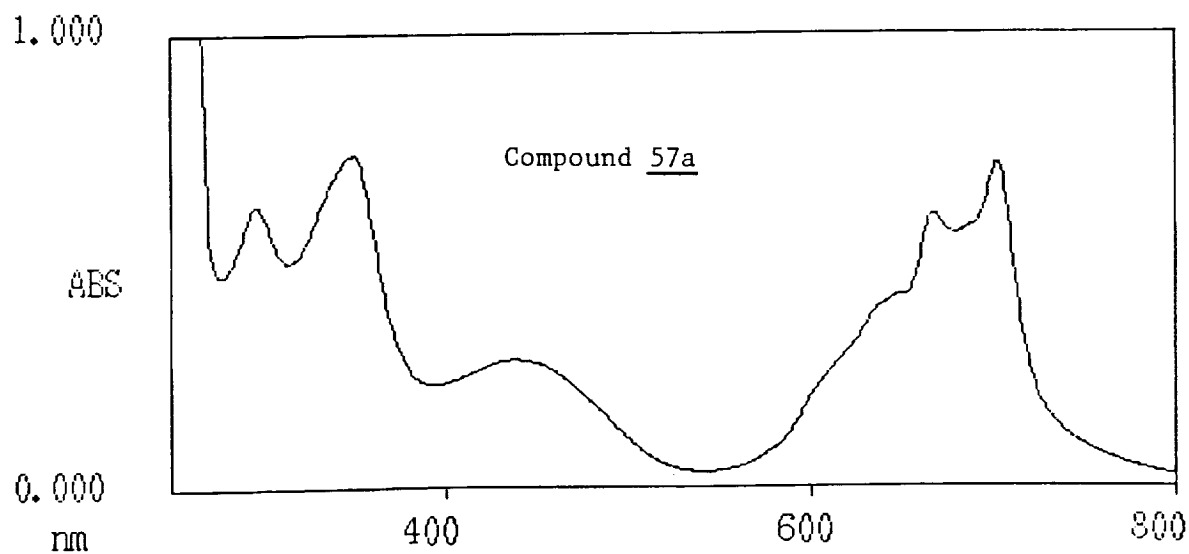
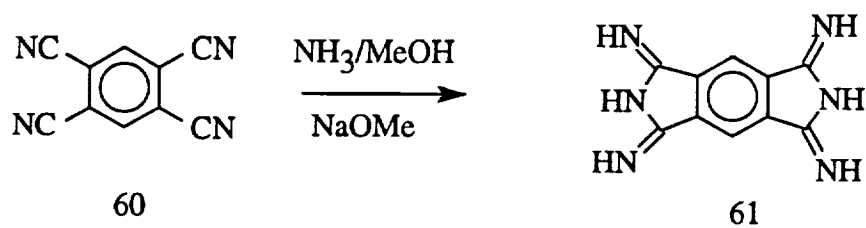
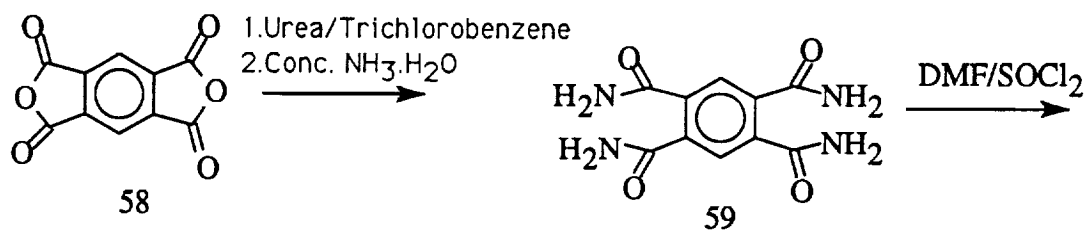
The original proposal targeted structures 54 and 55 as two bisphthalocyanines to possibly synthesize. Compounds of the type represented by Compound 51 have been published in the literature and are very stable. Compound 55 was targeted as our first goal. The attempts to produce 55 resulted in the formation of the bisimide Compound 4. This reaction path was confirmed by utilizing the heating of just urea and Compound 2 to produce the same identical product as that when phthalic anhydride was included. Therefore Compound 55 cannot be prepared by this classical methodology.

After considerable discussion with NASA, Compounds 52 and 53 were targeted as well as pursuing the naphthalene model for compound 55 to produce Compound 6.

### Benzene Core

The first bisphthalocyanine synthesized was based upon pyromellitic dianhydride. This compound is similar to that reported in the literature with the exception of the alkyl chain length is two carbons longer. This octadodecyl system Compound 51a was prepared by the method outlined below. Compound 58 was converted to Compound 61 which again is a key intermediate in the formation of phthalocyanines. Compound 61 was then heated with Compound 36 produce a mixture of Compound 37 and 51a, the single and double ring phthalocyanines.

The two ringed system is soluble in the typical solvents used to dissolve the polymers used in coatings as well as being compatible with the polymers themselves. We have working out separation technique using size exclusion chromatography which is capable of resolving the single from the double ringed phthalocyanine system. The use of size exclusion chromatography beads for preparative separation of these two materials worked well. The UV/Visible spectra of the mixture indicate a great similarity between the two compounds.



NO.	PEAK		VALLEY	
	nm	ABS	nm	ABS
1	702.0	0.713	678.0	0.559
2	667.0	0.600	541.0	0.033
3	438.0	0.282	394.0	0.228
4	351.0	0.734	314.0	0.499
5	297.0	0.624	277.0	0.468

### Naphthalene Core

The synthesis of the naphthalene core used in making compound 52a is shown below Compounds 62 - 67. The synthetic pathway worked well except for conversion of 65 to 66. Here the purification of the product was difficult. Conversion of 66 to the key intermediate 67 went well. Compound 67 was then heated with Compound 36 to produce Compound 52a and Compound 37, the double and single ringed systems. The separation of the two compounds was again accomplished with size exclusion chromatography. The spectra agreed well with the proposed structure as did its molecular weight. The UV/Vis spectra is given below. This synthesis represents the first naphthalene core bisphthalocyanine made.

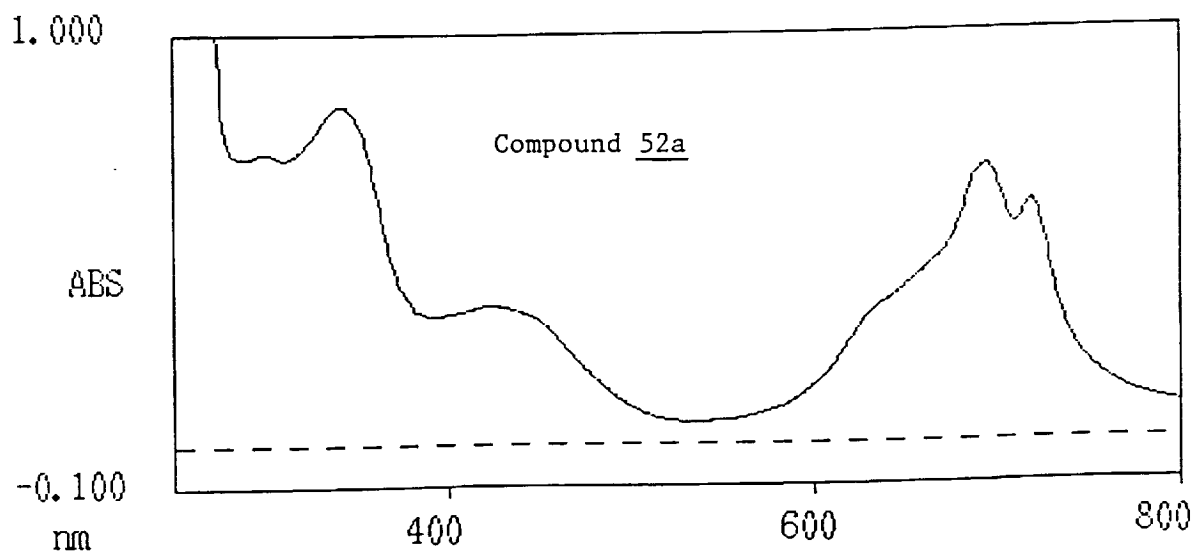
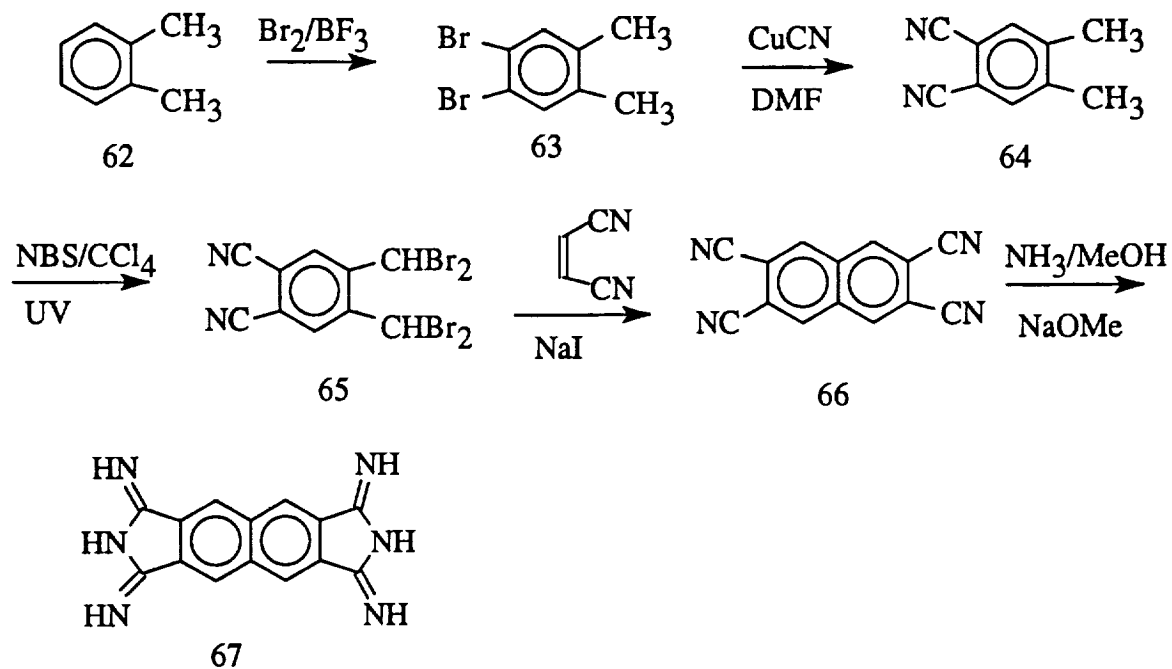
### Anthracene Core

Three major approaches were made to synthesize an anthracene core, Compound 83. These are depicted below in structures 62 to 83. The object was to synthesize Compound 53a.

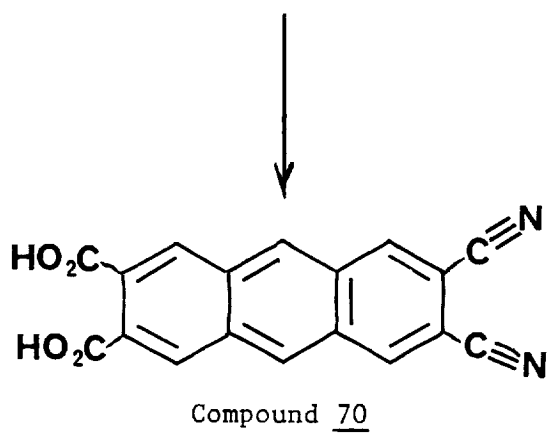
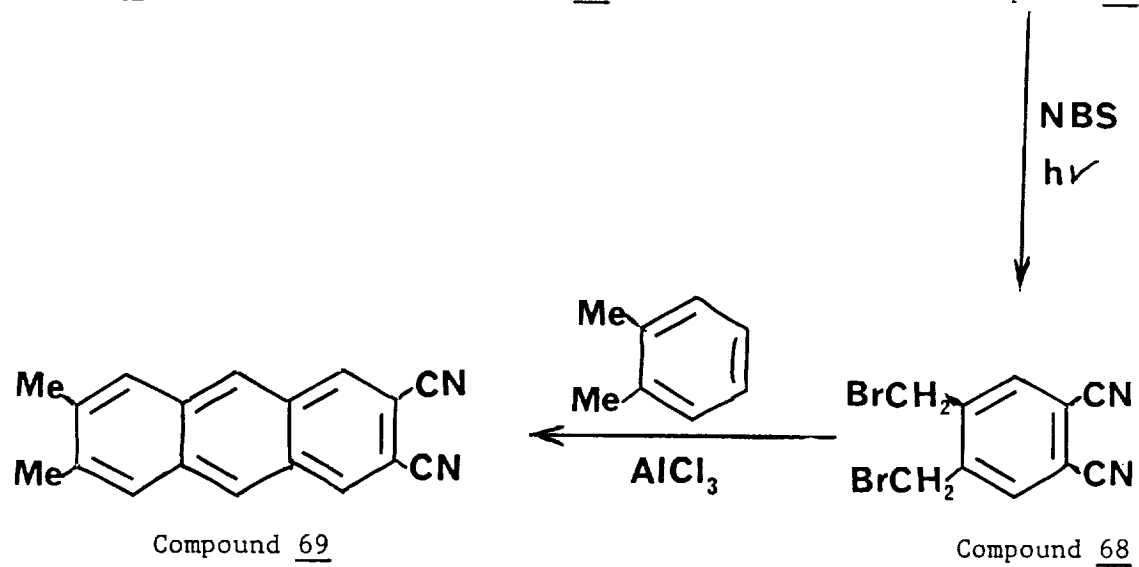
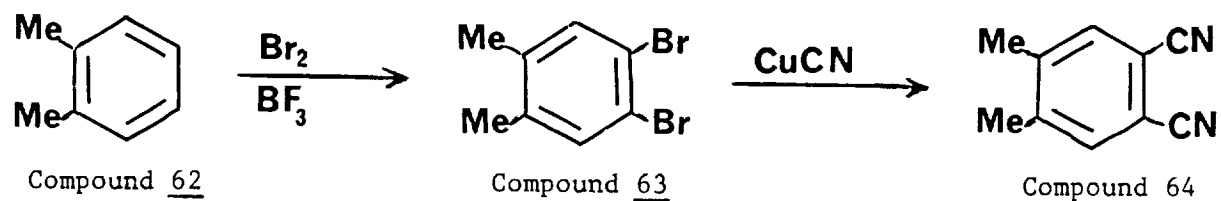
The first approach has progressed to structure 64 and on a small scale compound 68 has been made. This approach is of low yield and somewhat poor but effective. The purification of Compound 68 makes this approach somewhat less attractive.

The second approach is far more elegant utilizing a double Diels Alder of 71 and 72 to produce followed by air oxidation cleanly produced the dione 73. The oxidation of 73 using chromate in liquid carbon dioxide produced Compound 76. Compound 76 was also produced from a tetra-Friedel Craft reaction on ortho-xylene followed by chromate oxidation in liquid carbon dioxide. The two approaches were combined to increase the amount of Compound 76.

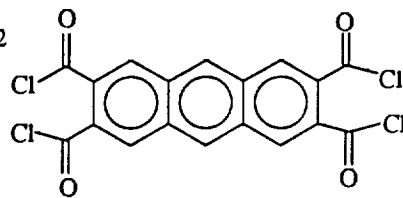
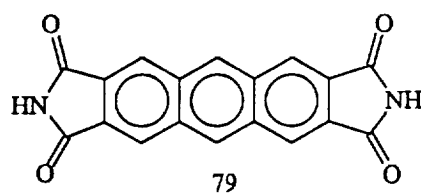
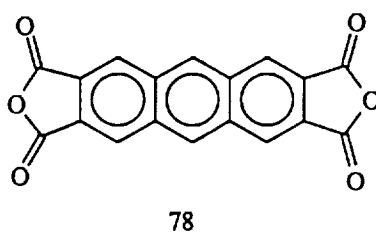
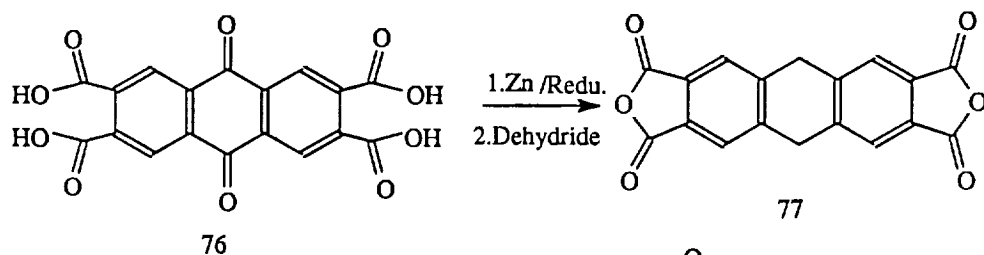
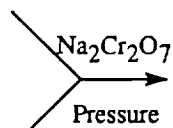
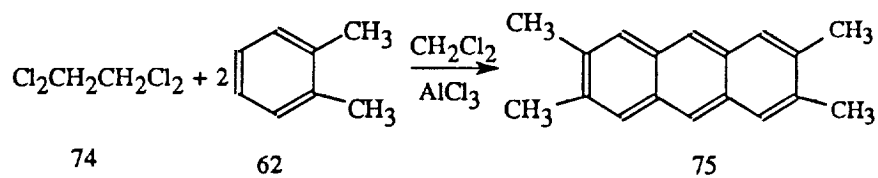
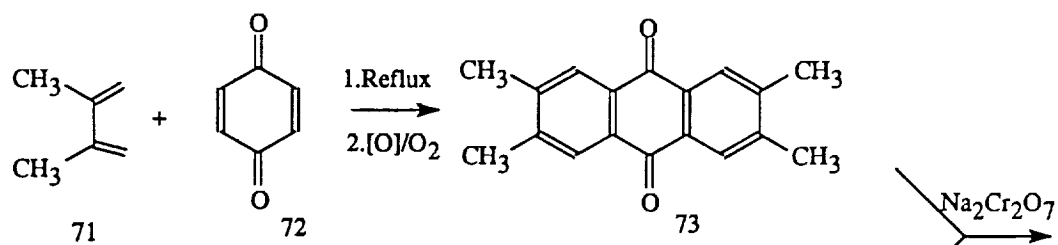
Compound 76 was then reduced and then dehydrated to form the bis-anhydride Compound 77. Aromatization and purification by sublimation produced the targeted anhydride Compound 78. It was planned that this less reactive compound would be converted to Compound 83. All attempts to convert this material to Compound 83 have failed. Compound 83 was reacted with Compound 36 in urea in hopes of the formation of Compound 53a, however no bisphthalocyanine was produced.



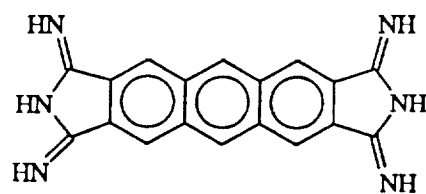
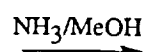
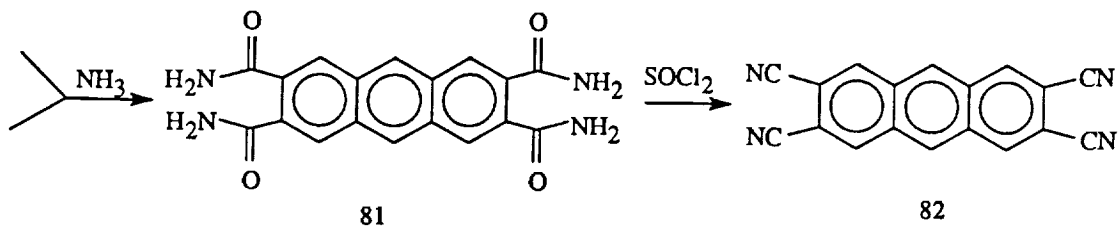
NO.	PEAK		VALLEY	
	nm	ABS	nm	ABS
1	720.0	0.583	710.0	0.529
2	694.0	0.671	535.0	0.055
3	424.0	0.339	393.0	0.315
4	341.0	0.827	310.0	0.700
5	299.0	0.715	288.0	0.701







80

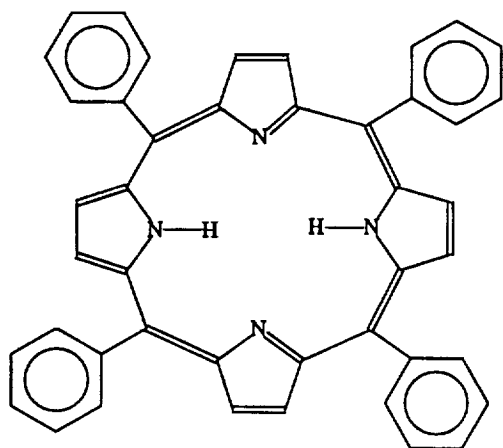


83

## PLASTIC UV PROTECTION

The design of the test procedure for the evaluation of the phthalocyanines for protecting plastics from UV damage are being made with no inhibitor, phthalo blue (commercial) and phthalo green (commercial) as standard materials for comparison with our new pigments. The materials are being tested as to gloss, color, molecular weight distribution and IR. After exposure to UV, the materials will be likewise evaluated by the same techniques. The these tests will be done by Diep Trinh at NASA.

We have prepared the phthalo blue, phthalo green and polystyrene standard glass test panels on samples as well as the single ringed phthalocyanine Compound 37 based on 1,2-didodecyloxy-4,5-dicyanobenzene for the photodegradation study. We are using polystyrene with a 3% loading of the pigments which are insoluble and 1.5% pigment for the newly synthesized soluble pigments. Polystyrene is known to yellow and degrade with UV exposure. We have prepared it in solution so that it can be applied to glass as a thin film for UV exposure. For comparison purposes we have prepared a set of samples using 0.75% tetraphenylporphine, Compound 84, as the soluble pigment. These are carbon analogues of the phthalocyanines and are soluble in the solvent used, toluene, and do not tend to form dimers in solution due to the four phenyls being at a  $45^\circ$  dihedral angle to the porphyrin ring. The color of this pigment is a maroon in solution or in the polymer film but purple in the crystalline solid form. The polymer/pigment system was milled in toluene with glass beads in a pseudo-sand mill (a straight blade on a drill press). We have observed a significant cobwebbing problem with the spraying due to the high molecular weight of the polystyrene we are using. This problem will not prevent the use of this system but does create a mess during the spraying process. The color development was very good but the long term solution stability of the insoluble pigments is not good. The dispersed pigments were sprayed within hours of their being milled. The samples were wrapped in plastic rap, and packaged for shipment. Five plates of each type of coating were made. A total of 25 samples were shipped UPS to Diep Trien.



## EXPERIMENTAL

Matheson high purity argon was used to maintain inert atmosphere conditions. Infrared(ir) spectra were recorded on Perkin-Elmer 1750 FT-IR spectrophotometer using KBr disc. Nuclear magnetic resonance(nmr) spectra were recorded on JEOL FX-100 multinuclear NMR using deuteriochloroform as the solvent and tetramethyl silane as the internal standard. The positions of the signal are reported in delta units. (The splittings of the signals are described as singlets(s), doublet(d), triplets(t), quartet(q), or multiplets(m)). The visible-ultraviolet spectra(UV) were recorded on a Hitachi 2000 spectrometer. Melting points(mp) were determined using Fisher-Johns melting apparatus. Thin-layer chromatography(TLC) was performed using alumina as the absorbent. Flash chromatography was performed using silica gel of particle size (40-63  $\mu$ m). All solvents were freshly distilled before use. DMF was passed through alumina column before use. Elemental analysis were performed by Galbraith Laboratories, INC, Knoxville, TN.

### *1,2-Bis(dodecyloxy)benzene (33)*

A solution of 44 g(0.40 mol) catechol in 150 ml of DMSO was deoxygenated by repeated evacuation followed by admission of nitrogen. 1-Bromododecane(210 g, 0.84 mol) was added and the two-phase system again deoxygenated. 125 g(0.9 mol) of  $K_2CO_3$  was then added and the mixture heated at 100°C in a dry nitrogen atmosphere with mechanical stirring. After 8 h, 500 ml of water and 200 ml of methylene chloride were added. The organic layer was separated and the aqueous layer extracted with 3x50 ml of chloroform. The combined organic extracts were washed with 200 ml of water, dried over  $MgSO_4$  and concentrated under vacuum. Excess 1-bromododecane was removed by distillation under reduced

pressure(134-135°C; 6 Torr). The remaining light-brown solid was recrystallized from acetone(4-7°C). Yield 134g (75%) of a white solid; m.p. 51 C. IR(KBr): 750(o-substituted benzene), 1020(ArOC)  $cm^{-1}$ .  $^1H$ NMR: 0.9(t, 6H,  $CH_3$ ), 1.3(s, br, 40H,  $CH_2$ ), 3.90(t, 4H,  $OCH_2$ ), 6.9(s, 4H, ArH).

### *1,2-Dibromo-4,5-bis(dodecyloxy)benzene (34)*

Compound 33 (102 g, 0.23 mol) and catalytic amount of  $BF_3$  was dissolved in 500 ml of Chloroform. To this solution 26 ml(0.50 mol) of  $Br_2$  in 50 ml of methylene chloride was added over 1 h, the first half at 0°C, the second half at room temperature. The mixture was stirred for 2 h at 25°C to complete the reaction, which was checked by TLC. The reaction mixture was washed with 10 % aqueous  $NaHSO_3$ , 10 % aqueous  $NaHCO_3$  and twice with water. The extract was dried over  $MgSO_4$  and evaporated to dryness. Recrystallization from methylene chloride yielded a white powder. Yield 131 g (94%); m.p. 53.8 C. IR(KBr): 654(ArBr), 1021(ArOC)  $cm^{-1}$ .  $^1H$ NMR: 0.90(t, 6H,  $CH_3$ ), 1.3(s, br, 40H,  $CH_2$ ), 3.93(t, 4H,  $OCH_2$ ), 7.07(s, 2H, ArH).

### *1,2-Dicyano-4,5-bis(dodecyloxy)benzene (35)*

A mixture of 202 g(0.33 mole) 1,2-dibromo-4,5-bis(dodecyloxy)-benzene(34) and 104 g(1.16 mole) CuCN was refluxed in 1400 ml DMF and 130 ml pyridine for 6 h under an atmosphere of dry nitrogen. After being cooled, the reaction mixture was poured into 4 l concentrated ammonium hydroxide and air was bubble through the solution for 20 h. The remaining solid was suction-filtered over sintered glass. The residue was washed with 10% aqueous ammonia until the filtrate was colorless. Subsequently, the solid was washed with water until the washings were neutral. The dry, crude product was extracted with ether for 48 h using a soxhlet apparatus. The extract was evaporated to dryness and the product recrystallized from cyclohexane. The purity of the product was checked with TLC(SiO<sub>2</sub>:eluent CH<sub>3</sub>, R<sub>f</sub>=0.5). Yield 78 g (47 %); m.p. 107°C. IR(KBr):2229(CN),1095(ArOC) cm<sup>-1</sup>. <sup>1</sup>H NMR:0.88(t, 6H CH<sub>3</sub>), 1.5(s, br, 40H, CH<sub>2</sub>), 4.05(t, 4H, OCH<sub>2</sub>), 7.11(s, 2H, ArH) Analysis: C<sub>32</sub>H<sub>52</sub>N<sub>2</sub>O<sub>2</sub> (496.8), calc. (%):C, 77.36;H, 10.55;N, 5.64. Found(%):C, 76.30;H, 9.89;N, 6.34.

### *1,3-Diimino-5,6-bis(dodecyloxy)-isoindoline (36)*

A rapid stream of gaseous ammonia is bubbled through a solution of 5 g(0.01 mole) 1,2-dicyano-4,5-bis(dodecyloxy)benzene (35) and 50 mg sodium methoxide in 50 ml absolute methanol at room temperature for 1 h. The solution is heated at reflux for a further 4 h, while the addition of ammonia is continued. At the end of addition, a precipitate is formed which is collected by suction after standing overnight and washed with small amounts of cold methanol; yield:5.1 g (98%);light green crystals which decompose at 125°C with green color(from methanol). IR(KBr):3215(N-H); 1602(C-N);1553(C-N);1039(ArOC)cm<sup>-1</sup>.

### *Pyromellitimide*

A mixture consisting of 20 g(0.09 mole) of pyromellitic anhydride, 18 g(0.3 mole) of urea, and 135 g of trichlorobenzene was heated at 130°C for several hours, then at 150-60°C for two h. The crude pink colored pyromellitimide did not melt below 310°C. Treatment of the crude amide with 150 ml aqueous ammonia at room temperature gave 15 g of nearly colorless pyromellitimide. The amide decomposed at 285°C.

### *Pyromellitonitrile (60)*

A stirred suspension of 2g(0.08 mole) pyromellitimide in 12 ml DMF was warmed to 60°C before 3.84 g (0.032 mole) thionyl chloride was added dropwise. After the mixture was heated to 7 h at 60°C, dilute hydrochloric acid was added to decompose unreacted thionyl chloride, and the mixture was filtered. The residue was washed with water until it was neutral to litmus and then was slurried four times in hot, glacial acetic acid and filtered hot. After cooling in refrigerator overnight, filter it and get tan solid. Recrystallization from ethanol. Yield:0.67g (47.26%);m.p.:264-267°C (same as literature);IR:2245(CN); 3113, 3048(CH);916(1,2,4,5-substitute) cm<sup>-1</sup>.

### Preparation of the bis-1,3-diiminoisoindoline(61)

A rapid stream of gaseous ammonia is bubbled through a solution of 2 g(0.01 mole) Pyromellitonitrile (60) and 0.6g sodium methoxide in 40 ml absolute methanol at room temperature for 1 h. The solution is heated at reflux for 4 h, while the addition of ammonia is continued. The precipitate formed is then collected by suction and washed with small amounts of cold methanol; yield: 2.4 g (100%) light green colored solid; m.p. >300°C. IR(KBr): 3358(N-H); 1639(C-N); 1560(C-N) cm<sup>-1</sup>.

### Binuclear phthalocyanine(51a) (& mononuclear phthalocyanine, 37)

1.5g(2.9mmole) of compound 36 and 0.026g(0.12 mmole) of 61, were heated at 150°C (oil bath) in 8 ml 2-N,N-dimethylaminoethanol for 70 h under an argon atmosphere. The mixture gradually changed color from light green to dark green. After cooling to room temperature, the mixture was diluted with acetone and the green colored residue was filtered. The residue was subsequently extracted in a soxhlet apparatus with acetone(24 h), methanol(48 h) and ether (24 h). The product was further purified by flash chromatography using 5x12 cm column. The green product was preadsorbed on silica and eluted with toluene to give monomeric 2,3,9,10,16,17,23,24-octakis(dodecyloxy)phthalocyanine, Compound 37, as a blue green solid after solvent evaporation. Further elution with 2-methoxyethanol/toluene(3/40) yielded after solvent evaporation a mixed of binuclear and mononuclear fraction. This fraction was further purified by gel permeation chromatography using a 3 cm wide column packed SX1 BioBeads 70 cm high. The mononuclear-Binuclear fraction was eluted with freshly distilled toluene. The faster moving band consisting of Binuclear species was further purified by flash chromatography using toluene/2-methoxyethanol (40/3) as eluent and gave 40 mg dark green Binuclear 51a (10 %) while the slower moving band of mononuclear, 37 species was not further purified. Analytical GPC column (THF as mobile phase) verified Binuclear 51a had less retention volume (i.e higher molecular weight) than mononuclear 37.

Binuclear 51a: IR: 3295(w, NH), 2854/2922(str, CH), 1607(NH), 1278(ArO), 1104(ArOC); <sup>1</sup>H NMR 0.92-2.11(br. CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub><sup>-</sup>), 4.58 (br, OCH<sub>2</sub>), 8.2(br, aromatic); UV/VIS(CHCl<sub>3</sub>) X<sub>max</sub>/nm[log E/dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup>]: 702(5.14), 667(5.07)

Mononuclear 37: IR: 3276(w, NH), 2850/2921(str, CH), 1611(NH), 1277(ArO), 1101(ArOC), 746; <sup>1</sup>H NMR: -2.5 to -2.9(br., 2H, NH), 0.93 - 2.15(br, 184H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub><sup>-</sup>), 4.50(br., 16H, OCH<sub>2</sub>), 8.46(br, s, 8H, ArH); UV/VIS(CHCl<sub>3</sub>) X<sub>max</sub>/nm[log E/dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup>]: 702(5.03), 665(4.94), 646(sh), 603(4.27).

*Synthesis bis-diiminoisoindoline, 67 from 2,3,6,7-tetracyanonaphthalene, 66*

A rapid stream of gaseous ammonia is bubbled through a solution of 0.1 g (0.87 mmole) 2,3,6,7-tetracyanonaphthalene, 66 and 17 mg sodium in 9 ml dry methanol/ dioxane (1/1) mixture at room temperature for 1 h. The solution is heated with stirring at 80°C for a further 2 h, while the addition of ammonia is continued. The brown colored material was obtained after vacuum pull out solvent, and the material was washed with small amounts of cold methanol; Yield: 0.104 g (90 %) brown colored solid; m.p. > 300°C. IR (KBr): 3333 (N-H); 1638 (C-N); 1542 (C-N) cm<sup>-1</sup>.

*Binuclear phthalocyanine (52a)*

The diiminoisoindoline, 67 obtained from 18 mg (0.079 mmole) 2,3,3,7-tetracyanonaphthalene, 66 and 1.0 g (1.9 mmole) 1,3-bisimino-5,6-didodecyloxyisoindoline, 36 were heated at 150°C (oil bath) in 7 ml 2-N,N-dimethylaminoethanol for 70 h under an argon atmosphere. The mixture gradually changed color from light green to dark green. After cooling to room temperature, the mixture was diluted with acetone and the green colored residue was filtered. The residue was subsequently extracted in a Soxhlet apparatus with acetone (24 h), methanol (48 h) and ether (24 h). The product was further purified by flash chromatography using 3x12 cm column. The green product was preadsorbed on silica and eluted with toluene to give monomeric 2,3,9,10,16,17,23,24-octakis (dodecyloxy)phthalocyanine, 37 as a blue green solid after solvent evaporation. Further elution with 2-methoxyethanol/ toluene (3/40) yielded after solvent evaporation a mixed of binuclear and mononuclear fraction. This fraction was further purified by gel permeation chromatography using a 3 cm wide column packed SX1 BioBeads 70 cm high. The mononuclear-Binuclear fraction was eluted with freshly distilled toluene. The faster moving band consisting of Binuclear species was further purified by flash chromatography using toluene/2-methoxyethanol (40/3) as eluent and gave 15 mg dark green Binuclear 52a (6%) while the slower moving band of mononuclear species was not further purified. Analytical GPC column (THF as mobile phase) verified Binuclear 52a had less retention volume (i.e. higher molecular weight) than mononuclear 37.

Binuclear 52a: IR: 3197 (w, NH), 2854/2923 (str, CH), 1603 (NH), 1278 (ArO), 1096 (ArOC); <sup>1</sup>H NMR 0.92-2.11 (br. CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>-), 4.58 (br, OCH<sub>2</sub>); UV/VIS (CHCl<sub>3</sub>) X<sub>max</sub>/nm [log E/dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup>]: 720 (4.55), 694 (4.62).

*Tetraphenyl-o-phthalonitrile* [46]

A solution of 12.8g(0.033 mole) tetraphenylcyclopentadienone, 44 and 2.8g(0.036 mole) furmarnitrile, 45 in 25 ml ml of bromobenzene was refluxed for 2 h. The reaction mixture was allowed to cool and then 8g(0.05 mole) of bromine in 8.5 ml bromobenzene was slowly added down and followed by refluxing for 3 h. Cooling gave a crop of crystals which was filtered and was washed with 7ml of cold toluene and the 7ml of cold petroleum ether(b.p. 90-100°C). The residue was recrystallized three times from toluene and three times from benzene to constant melting point affording colorless crystals. Yield:4.0 g(28%); m.p.:265°C (literature:265.3-265.4°C) IR:2227(CN);3057(CH)

*1,3-Diimino-4,5,6,7-tetraphenyl-isoindoline*, 47

A rapid stream of gaseous ammonia is bubbled through a solution of 2 g(4.6 mmole) Tetraphenyl-o-phthalonitrile, 46 and 0.4g sodium in 50 ml absolute methanol and 50 ml dioxane at room temperature for 1 h. The solution is heated with stirring at reflux for a further 4 h, while the addition of ammonia is continued. The yellow colored material was obtained after vacuum pull out solvent, and the material was washed with small amounts of cold methanol;yield:1.7 g (82%)light yellow colored solid; m.p.>300°C. IR(KBr):3325(N-H); 1654(C-N);1577(C-N) cm<sup>-1</sup>.

*1,2,3,4-Tetraphenyl-9,10,16,17,23,24-hexakis(dodecyloxy)phthalocyanine*, 48

0.5 g(1.1 mmole) crude 1,3-diimino-4,5,6,7-tetraphenyl-isoindoline in 10 ml of N,N-dimethylaminoethanol, 47 was heated to 150°C(oil bath) under an argon atmosphere. Compound 36, 0.57g(1.1 mmole), was then added over 5 portions within 5 h. The mixture was heated at 150°C for additional 70 h under an argon atmosphere. The mixture was cooled to room temperature, diluted with acetone, filtered, and washed thoroughly with methanol until the filtrate was almost clear. The crude product was extracted with methanol in a soxhlet apparatus to remove yellow impurities. The desired product was then extract 24 h with diethyl ether. The product was further purified by flash chromatography using 2-methyloxyethanol/toluene(3/40) give as a green solid.Through H NMR aromatic region integration ratio, it show that it was mainly mono-tetraphenyl substituted, 48 with some di-tetraphenyl substitution, 48a . Yield: 0.20 g(28% based on mono-tetrasubstitute 48). IR:3316(NH);2853/2922(str,CH);1105(ArOC)cm<sup>-1</sup>.HNMR:0.93-2.3 (m,br,CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>);4.32(s,OCH<sub>2</sub>);7.18-7.64(m,4ArH-Pc);8.57-8.66 (d,ArH).UV/Vis(CHCl<sub>3</sub>) Xmax/nm:700,678,640(sh),615.



### 1,8-Dibromonaphthalene, 31

A two liter three necked round bottom flask was charged with 26.7g (0.167 mole) of 1,8-diaminonaphthalene and 333 ml of 6.9M sulfuric acid. The suspension was cooled to  $-20^{\circ}\text{C}$  before adding 34.0g (0.493mole) sodium nitrite and 225 ml of water followed by a solution of 38.6g (0.269 mole) copper (I) bromide in 400ml hydrobromic acid. This mixture was brought to room temperature before heating to  $50^{\circ}\text{C}$  for 1 hour followed by heating overnight at  $40^{\circ}\text{C}$ . It was then heated for three hours at  $65^{\circ}\text{C}$  before cooling to  $0^{\circ}\text{C}$ . At this temperature, solid sodium hydroxide was added until basic. The mixture was extracted using THF (tetrahydrofuran) and diethyl ether. It was treated several times with charcoal in hexane. Finally it was crystallized three from dilute alcohol and animal charcoal [1] to give 1.31g of 1,8-dibromonaphthalene (yield 2.6%), m.p.  $106-108^{\circ}\text{C}$ ; IR spectrum was identical to the literature.

### 1,8-Dicyanonaphthalene, 26

1.3g (0.004mole) dibromonaphthalene, 31 was added to 11 ml DMF (dimethylformamide) followed by bubbling through nitrogen for 20 minutes. Copper (I) Cyanide (1.680g, 0.0187mole) was introduced and a nitrogen atmosphere was maintained. It was refluxed for four and a half hours. At first, it was bright yellow but became dark orange after two and a half hours. This mixture was added to 5.110g sodium cyanide in 120 ml water. The resulting solution was extracted with 4/100 ml portions of methylene chloride until colorless. Concentration of the extract was carried out and the crude 1,8-dicyanonaphthalene was crystallized from methylene chloride (fawn colored needles), m.p.  $231/232^{\circ}\text{C}$ . It was purified by sublimation and finally by recrystallization from alcohol (yield 75.2%) to give a light green solid, m.p.  $232/233^{\circ}\text{C}$ ; IR(KBr,  $\text{cm}^{-1}$ ): 2240, 2220 (CN). NMR ( $\text{CDCl}_3$ ) 8.45-7.40 (m, aromatic H).

### Preparation of 11

0.5400g (2.8mmole) of 1,8-dicyanonaphthalene, 26 was added to 42 ml sodium in 50 ml solvent (25ml methanol, 25 ml dimethoxymethane). Ammonia was bubbled through for one hour at room temperature. The temperature was increased to  $80^{\circ}\text{C}$  for three and a half hours before a sample was taken which showed no peak at  $2240\text{cm}^{-1}$  or 2220 and thin layer chromatography indicated the absence of starting material. Diethyl ether was used as eluent but was unable to separate the product from the other materials so tried chloroform and got very good separation. The reaction mixture was stored overnight in the freezer under nitrogen to increase crystallization but ended up pulling a vacuum to remove the solvents. It was passed through an alumina column after adding acetic acid and the fractions were collected. They were washed with water and methanol to remove the acetic acid. Further column chromatography was necessary with methanol as the solvent. Separation was achieved. Yield 51%; m.p.  $>265^{\circ}\text{C}$ ; IR( $\text{cm}^{-1}$ ): 3500-3290(w), 2922(s), 2870(w), 1568(s), 1460(m);  $^1\text{H}$ NMR: 8.52-8.59 (d, aromatic H), 8.27-8.40 (t, aromatic H) and 7.64-7.84 (t, aromatic H).

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## CONCLUSIONS

The project has seen a number of significant milestones reached. The first is the successful synthesis of a new bisphthalocyanine based upon a naphthalene core. The second milestone was the synthesis of the key 1,8-naphthalene intermediate Compound 11. This compound is the key to a new and unique class of phthalocyanine. Compound 11 is the first example of its type and the first amine/imine tautomer to be isolated. The proton and carbon thirteen NMR's illustrate that this compound does not tautomerize rapidly on an NMR time scale as had been proposed previously in the literature.

The isolation of a green, stable new compound based upon Compound 11 is the first of its type to be synthesized. It represents a new series of chemicals which may poses unique catalytic, conductivity or photochemical properties.

The work on these structures represents several breakthroughs and firsts. The integral use of molecular modeling including quantum mechanics with synthesis has proven that the combination is the best approach to technological advancement of this area. We have found barriers, stable targets and interpreted results which would not have been possible without molecular modeling or without the synthetic results.

The photochemical degradation inhibition of plastics by phthalocyanine compounds has been initiated. Numerous samples of polystyrene pigmented with various potential inhibitors have been sent to NASA for testing and evaluation.

Several manuscripts will be produced over the next few months as final spectra, analysis and confirmation of the reactions, yields and some details are completed. These manuscripts will be submitted to NASA prior to publication.

The future of this area is very bright. The new class of compounds containing one 1,8-naphthalene system must be expanded and further evaluated. The electrochemistry of systems containing the naphthalene core must be explored to evaluate electron transfer communication differences between it and the benzene core system. Once the UV degradation results are analyzed on the samples sent to NASA, further work will be required to optimize these pigments as UV damage inhibitors.